Dynamic Response of Reflectivity of Metal/GeS₂ Systems during Laser Irradiation in Nanosecond Range

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Abstract- We constructed an equipment for measuring rapid changes in reflectivity of optical recording materials on test pieces during recording laser irradiation, which is very important in a development of these kinds of materials, with a time resolution less than 10 ns. Using this equipment, we examined the metal/GeS₂ systems in the performance as recording materials for Write Once Read Many (WORM) optical disks. Seven kinds of metals were tested. Differences in the profiles of the reflectivity changes during the laser irradiation were clearly elucidated depending on the metal layer materials. In/GeS₂ and Sn-Bi/GeS₂ (Sn-Bi: Sn-57wt%Bi eutectic alloy) samples showed the most rapid decreases in the reflectivity with low laser power absorbed in the samples. These results suggest that In/GeS₂ and Sn-Bi/GeS₂ are promising for the WORM optical recording material with high sensitivity and high recording speed.

Key words: reflectivity change, recording material, GeS₂, metal, In, Sn-Bi alloy, WORM optical disk, nanosecond

1. Introduction

In the initial stage of the development of new optical recording materials, it is generally not important for the candidate materials to fulfill the detailed specifications of final applications or media types. It is rather important to screen the candidates of new optical recording materials by making relative comparison of the fundamental properties such as reflectivity, modulation, minimum laser irradiation powers necessary to form recording pits, and recording speed¹⁾⁻³⁾. For evaluating these specifications, we constructed a equipment with which rapid changes in reflectivity during laser irradiation can be measured on test pieces of materials.

It is already known that chemical reaction between metals and GeS₂ are induced by laser irradiation⁴⁾. In this metal/GeS₂ system, both sulfurization of the metal layer and desulfurization of the GeS₂ layer bring about a decrease in the reflectivity. And the metal layer gives high reflectivity in as-deposited state. Therefore this system can be one of the candidate for WORM optical disks. Melting of the metal by laser heating can also contributes to decrease the reflectivity⁵⁾. We examined the metal/GeS₂ systems as recording materials of

WORM optical disks by measuring reflectivity changes during the laser irradiation with time resolution of less than 10 ns.

2. Experiment

2.1 The equipment for measurements of rapid reflectivity changes on test pieces

The schematic diagram of the equipment for measuring the rapid reflectivity changes was shown in Fig.1. The equipment consists of a laser diode system, a detecting system, a focusing system and several optical elements. The photograph around the sample holder was shown in Fig.2. The laser of a rectangular pulse with a wavelength (λ) of 830 nm from the laser diode system passes through a polarization beam splitter (PBS), a quarter-wave plate and an objective aspherical lens of silica glass, and focuses onto the samples. After reflected by the sample the laser beam travels along the same pass to return to the PBS. Then, the laser beam reaches to the detecting system. The specifications of the equipment were summarized in Table 1.

The laser irradiation power onto the samples was changed from 3.2 to 125 mW. When the injection

Fig.1 The schematic diagram of the constructed equipment for measuring rapid reflectivity changes.

current from the power supply to the laser diode was weaker, the rise time of the injection current became longer, resulting in a longer rise time of the irradiation power. To avoid this, neutral-density filters were used to adjust the laser irradiation power lower than 40 mW. The typical observations of the irradiated areas with an optical microscope were shown in Fig.3.

The time sequence data from the digital oscilloscope was normalized by simultaneously monitoring of the emitting laser power to compensate of fluctuation of the irradiation power. Then, the normalized data was filtered for noise reduction using FIR (Finite Impulse Response) low pass filter (cut-off frequency : 200 MHz, the number of FIR coefficient : 101, using von Hann window).

Fig.2 The photograph round the sample holder.

Fig.3 The typical observations of the irradiated areas with an optical microscope after 500 ns laser irradiation. The irradiation powers are (a)115 mW, (b) 29 mW.

2.2 Preparation of glass/metal/GeS₂ structure samples

Test piece samples of the metal/GeS₂ systems (Fig.4) were prepared by depositing metal layers succeeded by depositing GeS₂ layers by electron-beam evaporation onto Corning #7059 glass substrates with optical-flat surfaces. Cu, Ag, Au, Al, In, Sn and Sn-57wt%Bi eutectic alloy (Sn-Bi) were tested as metal layer materials. The metal layer thickness was 40 nm. The GeS₂ layer thickness was 70 nm in order to attain approximately $\lambda/4$ optical thickness for high absorbance. The deposition rates of the metals and GeS₂ were 0.5 nm/s and 1 nm/s, respectively. The laser beam was irradiated from the GeS₂ side in the measurements.

Initial optical properties (transmittance, reflectivity, absorbance) of the samples at $\lambda = 830$ nm measured with a spectrophotometer are shown in Table 2. The absorbance was obtained in the following manner: (100 - transmittance - reflectivity) (%). The melting points of the metals are also shown in Table 2.

Table 1 Specifications of the equipment.

laser wavelength	830 nm
max. irradiation power	125 mW (at the sample)
diameter of the laser beam at the sample	$\sim \phi 1 \mu\text{m}$
numerical aperture of the objective lens	0.68
synthetic resolution	≤ 10 ns
power supply	rise time, fall time ≤ 2 ns
pulse generator	max. frequency : 250 MHz, min. pulse duration : 2 ns rise time, fall time ≤ 1 ns
detector (silicon photo diode)	rise time, fall time ≤ 1 ns
digital oscilloscope	bandwidth : 500 MHz, max. sample rate : 2.5 G Sample/s

Fig.4 Metal/GeS₂ system samples.

Table 2 Optical properties of the samples and melting points of the metals.

metal layer material	Cu	Ag	Au	Al	In	Sn	Sn-Bi
transmittance (%)	30	9	15	1.2	8	11	9
reflectivity (%)	29	82	70	56	45	48	21
absorbance (%)	42	8	15	42	47	41	70
melting point (°C)	1083	961	1063	660	156	232	139

3. Results and Discussion

The measured reflectivity changes are shown in Fig. 5. The reflectivity was normalized so that the value before the laser irradiation equals unity. The values on the right side indicate the laser powers absorbed in the samples, that is, the irradiation power times the absorbance. The laser pulse duration was 1400 ns for all the samples. Figure 5(a) shows the results for the sample using Ag as the metal layer material. Almost no change was observed, even at the absorbed power, 10 mW, which corresponds to the maximum irradiation power, 125 mW. Figure 5(b) shows the results for the sample using Au. No change was observed at the absorbed power, 6.8 mW. When the absorbed power was higher, smaller decrease in the reflectivity was observed. When the absorbed power was 14 mW or larger, the reflectivity showed rapid remarkable decrease to 0.2-0.6 after small decrease described above. Figure 5(c) shows the results for the sample using Sn-Bi. The profiles of the reflectivity changes were different from those for the samples using Ag or Au. The reflectivity immediately started to decrease remarkably to 0.2-0.6 even at the weakest absorbed power, 4.5 mW.

As for the Au sample, the time duration where the reflectivity doesn't change remarkably was observed. After that, the remarkable decreases in reflectivity started. This indicates that it takes a long time to heat the sample to the temperature, T_r , at which the remarkable decrease in the reflectivity starts. On the contrary, the results for the Sn-Bi sample did not show such time duration as Au within the time resolution of the equipment. The reflectivity immediately started to decrease remarkably, due to lower T_r and/or lower thermal conductivity than Au.

Figure 6 shows the comparison of the results for the seven kinds of the samples where the absorbed power was the same for all the samples, 10 mW. The samples using Al, Ag, Au and Cu as the metal layer materials showed the similar profiles; small decreases in the reflectivity to 0.9 at most were observed. On the contrary the samples using In, Sn and Sn-Bi as the metal layer materials showed large decreases in the reflectivity to 0.5-0.6. These three kinds of metals have lower melting points. Therefore, melting of the metal layers

probably enhanced the decreases in the reflectivity. In comparison with the profiles of the samples using the three kinds of metals between 0-200 ns, In and Sn-Bi samples showed the most rapid decreases in the reflectivity. Therefore, In/GeS₂ and Sn-Bi/GeS₂ are the most promising materials for the optical recording materials for WORM optical disks with high sensitivity and high speed.

(a) Ag/GeS₂ sample

(b) Au/GeS₂ sample

(c) Sn-Bi/GeS₂ sample

Fig.5 Reflectivity changes of (a) Ag/GeS₂, (b) Au/GeS₂, (c) Sn-Bi/GeS₂ samples during the laser irradiation.

Fig.6 Reflectivity changes of the metal/GeS₂ system samples during the laser irradiation (absorbed power: 10 mW) .

4. Conclusion

We constructed an equipment with which rapid changes in the reflectivity during the recording laser irradiation on the test pieces with a time resolution less than 10 ns. Using this equipment we examined the

metal/GeS₂ system samples in the performance as WORM optical recording materials. Differences in the profiles of the reflectivity changes were clearly elucidated depending on the metal layer materials. In/GeS₂ and Sn-Bi/GeS₂ showed the most rapid decreases in the reflectivity among the seven kinds of samples at the same absorbed power. This result suggests that In/GeS₂ and Sn-Bi/GeS₂ are promising for the recording materials for WORM optical disks with high sensitivity and high recording speed. We believe that this equipment is useful to develop new optical recording materials.

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