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Research Report

Measurement of Change of Reflectance of Metal/GeS_2 Systems during Laser Irradiation with Nanosecond Time Resolution

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金属／GeS_2系のレーザー照射中におけるナノ秒分解能での反射率変化測定

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Abstract

We constructed an apparatus for measuring rapid changes in reflectance of optical recording materials during a recording laser irradiation with a time resolution of less than 10 ns. This newly constructed apparatus enabled rapid screening of material candidates, using not optical disc samples but rather small flat test pieces. We applied the apparatus to the metal candidates in GeS_2/metal bilayer systems for recordable optical discs. Differences in the profiles of the reflectance changes during the laser irradiation were clearly elucidated depending on the metal layer materials. GeS_2/In and GeS_2/Sn-Bi (Sn-Bi: Sn-57wt.%Bi eutectic alloy) samples showed the largest and the most rapid decreases in the reflectance with low laser power absorbed in the samples. These results were consistent with those of the examination using optical disc samples.

Keywords: Optical memory, Recordable optical disc, GeS_2, Metal, Reflectance, Change, Time resolution, Nanosecond

要　旨

記録レーザー光が照射される間の光記録材料の反射率変化を10 ns 以下の時間分解能で測定，評価できる装置を作製した。この装置により，光ディスクまで作らなくとも小さなテストピースを用いて，候補材料をスクリーニングすることが可能となった。この装置を用いて，GeS_2/金属積層膜の追記型光ディスク用記録材料としての性能を調べた。レーザー照射中の反射率変化のプロファイルが金属層材料の種類によって明らかに異なる様子が観測された。GeS_2 /In および GeS_2 /Sn-Bi (Sn-Bi：Sn-57wt.%Bi共晶合金) の試料は，低いレーザーパワーで最も大きく速い反射率の変化を示した。これは，光ディスク試料を用いた評価結果と一致する結果であった。

キーワード　光記録，追記型光ディスク，GeS_2，金属，反射率，変化，時間分解能，ナノ秒

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1. Introduction

In the initial stage of development of new optical recording materials, it is important to screen the candidates by comparing fundamental properties such as reflectance, modulation, minimum laser irradiation power necessary to form recording pits, and recording speed.[1-3] For this screening, we constructed an apparatus to measure rapid changes in reflectance during recording laser irradiation, not on optical disc samples, but rather on small flat test pieces (typically several cm^2) of optical recording materials. This made it more convenient and faster to survey different materials, layer thicknesses, and preparation conditions.

We used this apparatus to study GeS_2/metal bilayer systems as new class of optical recording materials for recordable optical discs being developed by ourselves. We have already found that the interfacial chemical reaction between GeS_2 and the metals, that is, desulfurization of GeS_2 and sulfurization of the metals is induced by intense laser irradiations.[4] The interfacial reaction degrades the high reflectance of the metal layer and high transparency of the GeS_2 layer. We have realized optical disc samples using the GeS_2/In and the GeS_2/Sn-Bi (Sn-Bi: Sn-57wt.%Bi eutectic alloy) showing good recording sensitivity that is nearly compatible with the commercially-available CD-R.[5, 6] In the present study, we measured the reflectance changes of the GeS_2/metal systems using In, Sn-Bi as well as other several kinds of metals for comparison during the recording laser irradiations in order to determine why the GeS_2/In and the GeS_2/Sn-Bi disc samples showed such good performance.

2. Experimental

2. 1 Apparatus to measure rapid reflectance changes of test pieces in sub-msec range

Figure 1 shows the schematic diagram of the apparatus. The apparatus consists of a laser diode system, a detection system, an auto-focusing system and several optical elements. The photograph near the sample holder is shown in **Fig. 2**.

The laser beam of a rectangular pulse with a wavelength (λ) 830 nm from the laser diode is collimated into a circular beam (5 mm in diameter) by the collimate lenses and the anamorphic prism pair. Then the laser beam passes through the

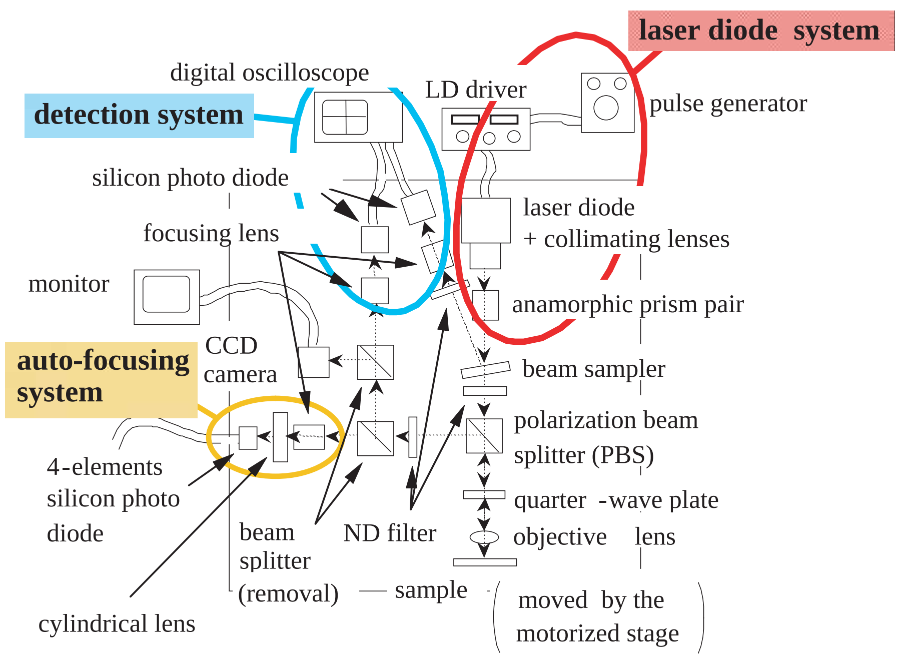

Fig. 1 Schematic diagram of the apparatus for measurement of rapid reflectance changes of recording materials.

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polarization beam splitter and the quarter-wave plate, and is focused onto the sample as a spot of approximately 1 μm in diameter by an objective aspherical lens of silica glass. After being reflected by the sample, the laser beam travels along the same path to return to the polarization beam splitter. Because the polarization direction of the reflected laser beam is changed to be perpendicular to that of the incident light, the reflected laser beam reaches the detection system. The intensity of the reflected laser beam is measured with the silicon pin-photodiode and the digital oscilloscope. The synthetic time resolution of the apparatus was less than 10 ns. The other specifications are summarized in **Table 1**.

After the sample is set on the sample holder, the laser beam of very weak intensity is incident on the sample, and the reflected light is introduced into the auto-focusing system for the sample to be located on the focal plane of the objective lens. The laser irradiation power directed onto the sample was changed from 3.2 to 125 mW with the irradiated location in the sample automatically changed. When the injection 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. After measuring the change in the reflectance during the laser irradiation, the irradiated area of the sample can be observed by introducing the reflected laser beam into the CCD camera. Typical observations of the irradiated areas are shown in **Figs. 3**(a) and (b). The time sequence data from the digital oscilloscope used in the detection system was normalized using the emitting laser power simultaneously monitored to compensate fluctuation of the irradiation power. Then, the normalized data was filtered for noise reduction using a Finite Impulse Response (FIR)

Table 1 Specifications of the equipment.

laser diode (SDL, 5431-G1)	wavelength : 830 nm max. emitting power : 200 mW modulation bandwidth : 1 GHz
power supply (ASAHI DATA SYSTEMS, ALP-7032PC)	max. injection current : 300 mA rise time, fall time ≦ 2 ns
pulse generator (tektronix, PG502)	max. frequency : 250 MHz, min. pulse duration : 2 ns rise time, fall time ≦ 1 ns
objective lens (Geltech, 350330)	numerical aperture : 0.68
Si pin photodiode (THORLABS, DET210)	rise time, fall time ≦ 1 ns active area : 0.8 mm^2
digital oscilloscope (tektronix, TDS644B)	bandwidth : 500 MHz, max. sampling rate : 2.5 G Sample/s
max. irradiation power irradiating beam diameter at sample synthetic time resolution	125 mW ~ ϕ 1 μm ≦ 10 ns

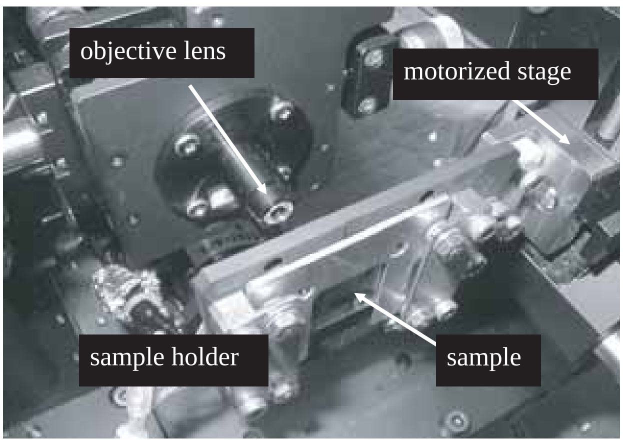

Fig. 2 Photograph around the sample holder.

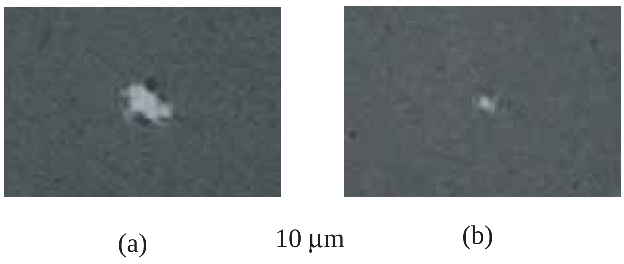

Fig. 3 Typical observations of the irradiated areas after 500 ns-laser irradiations. The irradiation powers were (a)115 mW, and (b) 29 mW.

low-pass filter (cut-off frequency: 200 MHz, the number of FIR coefficient: 101, using von Hann window).

2. 2 Preparation of GeS_2/ metal samples

Test pieces of the GeS_2/metal systems were prepared by electron-beam evaporation on Corning #7059 glass substrates of 2 cm^2 with optical-flat surfaces. In our previous work, it was found that an unintended reaction at the GeS_2/metal interface occurred when the substrate/GeS_2/metal systems were formed by successive depositions, resulting in a decrease of the reflectance.[6] To avoid the reaction during the depositions, the metal layer was firstly deposited to form the substrate/metal/GeS_2 structure as shown in **Fig. 4** in the present work. The samples were irradiated from the GeS_2 side in the measurements.

Besides In and Sn-Bi, Ag, Au, Cu, Al and Sn were tested as metal layer materials for comparison. The metal layer thickness was set to be 40 nm. The GeS_2 layer thickness was set to be approximately the $\lambda/4$ optical thickness of 70 nm to attain high absorbance. Transmittance and reflectance of the samples at λ=830 nm were measured using a spectrophotometer before laser irradiations. The results are shown in **Table 2**. Absorbance was obtained as 100-transmittance-reflectance [%]. The melting points of the metals are also shown in Table 2.

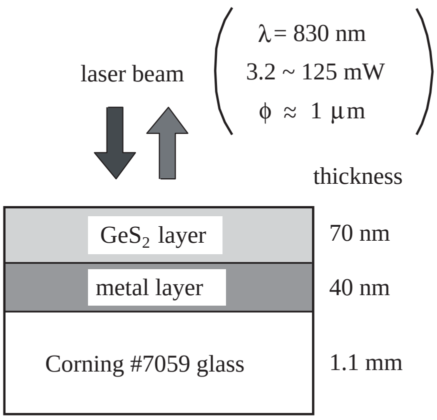

Fig. 4 Schematic of the GeS_2/metal samples.

Table 2 Optical properties of the GeS_2/metal 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
Reflectance (%)	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

Figures 5-7 show the changes of the measured reflectance normalized by the value before the laser irradiation. The laser pulse duration was 1400 ns for all the samples. The 'absorbed power' in the figures stands for the incident laser power times the

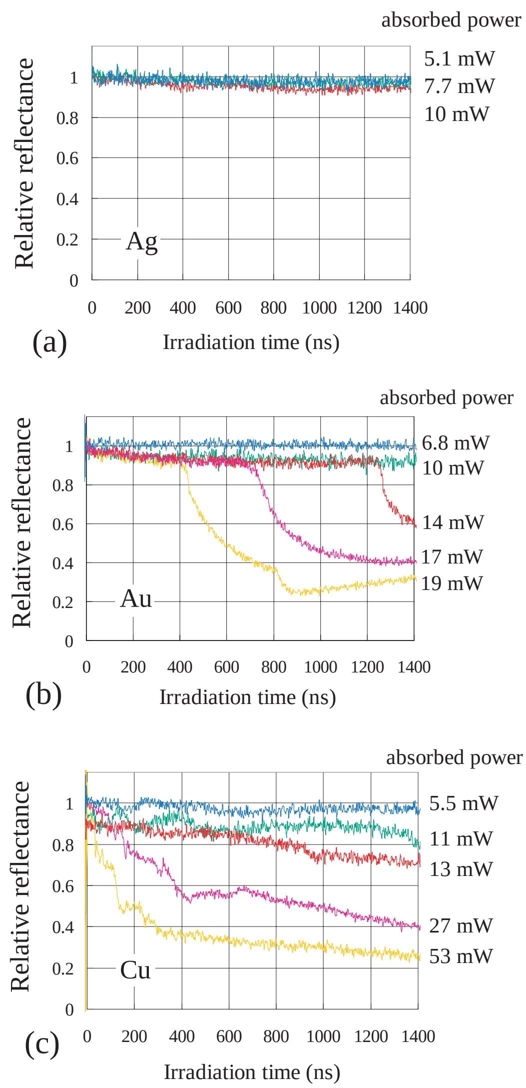

Fig. 5 Reflectance changes of the (a) GeS_2/Ag, (b) GeS_2/Au, and (c) GeS_2/Cu samples during the laser irradiations.

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absorbance.

Figures 5(a)-(c) show the results for the samples using (a) Ag, (b) Au and (c) Cu. Figure 5(a) for Ag showed only slight decreases, even at an absorbed power of 10 mW caused by the maximum incident laser power of 125 mW. Figure 5(b) for Au showed no change at 6.8 mW and a slow, but apparent, decrease at 10 mW. At 14 mW and greater, the sudden decreases in the reflectance to 20-60% after some duration were observed. These results indicate that incubation periods of several hundreds of nanoseconds are necessary for the sample to be heated to ignite the interfacial reaction. In Fig. 5(c) for Cu, incubation periods are observed but are diminished by larger and more rapid decreases of reflectance with increasing absorbed power.

The Al sample produced irregular fluctuations as shown in Fig. 6.

Figures 7(a)-(b) show the results for the Sn, In and Sn-Bi. In Fig. 7(a) for Sn, incubation periods are seen at 5.3-10 mW but are diminished by larger and more rapid decreases of reflectance with increasing absorbed power beyond that shown in Fig. 5(c) for Cu. Figure 7(b) for In showed a much more rapid decrease in reflectance than Sn but the general behavior resembles In and Cu. Figure 7(c) for Sn-Bi shows immediate decreases followed by certain gains in reflectance at the absorbed power of 9.1 mW or beyond.

Figure 8 shows the comparison of the results for the seven different metal layers, where the absorbed power was approximately 10 mW for all the samples. For Ag, Au, Cu and Al, the profiles are

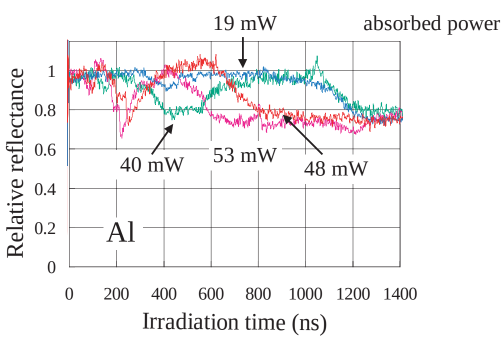

Fig. 6 Reflectance changes of the GeS_2/Al sample during the laser irradiations.

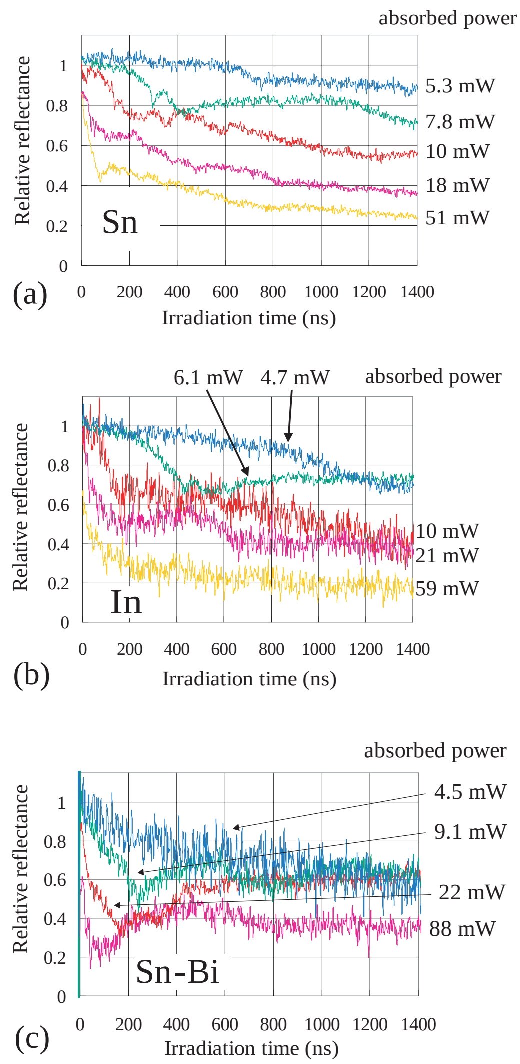

Fig. 7 Reflectance changes of the (a) GeS_2/Sn, (b) GeS_2/In, and (c) GeS_2/Sn-Bi samples during the laser irradiations.

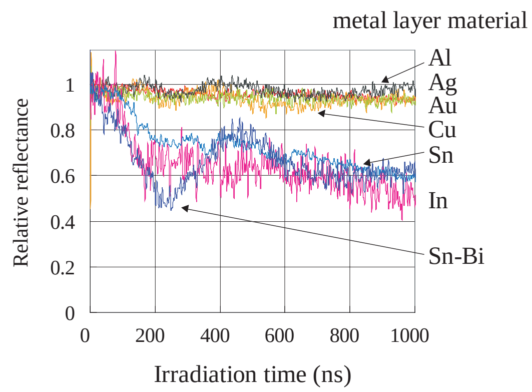

Fig. 8 Comparison of the reflectance changes of the GeS_2/metal samples during the laser irradiations at an absorbed power of 10 mW.

similar to each other. On the contrary for Sn, In and Sn-Bi, larger decreases in reflectance to 0.5-0.6 took place. These three metals have lower melting points than the former four metals, suggesting that melting contributed to the rapid and significant reflectance change. In general, a chemical reaction between two different substances becomes more active when one of the substances melts.[7] In addition, thermal conductivity of many metals[8] sometimes decreases to 0.5. Thus the dissipation of the heat generated by the laser absorption in the sample might be reduced, resulting in a rapid temperature rise and a promotion of the reaction between GeS_2 and the metals.

Among the three, In and Sn-Bi samples showed more rapid decreases in reflectance than Sn from 0 to 200 ns.

We have already revealed that GeS_2/In and GeS_2/Sn-Bi are promising materials for recordable optical discs with high recording sensitivity[5, 6] by testing optical disc samples. The present results, which are based on small-size test pieces, support the above choices of metals and elucidate the phenomenon that occurs during laser irradiation. The high sensitivities of the disc samples are thought to have originated from the rapid and large change in the reflectance from the present study.

4. Conclusion

We constructed an apparatus with which rapid changes in the reflectance during the recording laser irradiation on the test pieces with a time resolution of less than 10 ns. Using this apparatus we examined the GeS_2/metal system samples using seven metals for optical recording materials. We found that GeS_2/In and GeS_2/Sn-Bi are the most promising, showing the largest and the most rapid decreases in the reflectance at a certain absorbed power. These results were consistent with those of the examination using optical disc samples. We believe that this apparatus is useful to accelerate the development of the new optical recording materials.

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