Magnetic properties of Mn-Zn ferrite thin films fabricated by pulsed laser deposition

Hideki Etoh1,2, Junichi Sato2, Yoshiteru Murakami3, Akira Takahashi2 and Ryoichi Nakatani1

1 Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

2 Advanced Technology Research Laboratories Corporate Research and Development Group, Sharp Corporation, 2613-1 Ichinomoto-cho, Tenri, Nara 632-8567 Japan

E-mail: etoh-hideki@sharp.co.jp

Abstract. We investigated the basic properties of Mn-Zn ferrite thin films fabricated by pulsed laser deposition (PLD) with the aim of controlling their saturation magnetizations ($M_s$) and electrical resistivities. The $M_s$ and electrical resistivities varied dependent on the substrate temperature during deposition and post-anneal conditions. X-ray diffraction (XRD) measurement revealed the difference is due to the formation of a Mn-Zn ferrite and an Fe₂O₃ phase, which is attributed to the amount of oxygen in the post-anneal atmosphere.

1. Introduction

In the field of magnetic recording, a thermally assisted magnetic recording method is proposed to overcome the thermal agitation limit of recording media to achieve a higher recording density beyond Tb/inch² [1]. In this method, it is important to apply the magnetic recording field and the laser beam to the same position on the recording media. Although it is effective to incorporate a magnetic core in the recording head to apply a sufficiently large recording field, the core could possibly interfere with the optical path of the laser beam. Mn-Zn ferrite is a transparent magnetic material with a high $M_s$ and high resistivity [2]. It is a candidate for use as a magnetic core that will not interrupt the laser beam. In this paper, we report basic properties of Mn-Zn ferrite thin films fabricated by PLD. The aim is to adopt this material as the magnetic core of a thermally assisted magnetic recording head.

2. Experiment

Mn-Zn ferrite thin films were fabricated by PLD using a Nd:YAG laser at a wavelength of 266 nm and operated at 10 Hz at a pressure of $1 \times 10^{-4}$ Pa. The target was an oxide ceramic of Mn-8at%, Zn-23at%, Fe-69at%. Films were deposited onto Si substrates with oxidized surfaces. The target and substrates were rotated during depositions. The film thickness was fixed at 50 nm. We tested various procedures of fabricating samples. In one procedure samples are deposited with a substrate temperature of 350 to 500 °C and not annealed after deposition, in another procedure samples are deposited at room temperature and annealed after deposition at a pressure of $1 \times 10^{-4}$ Pa with an annealing temperature of 350 to 500 °C for 20 minutes, and in the other procedure samples are deposited at room temperature and annealed after deposition in an air atmosphere with an annealing temperature of 350 to 500 °C for...
5 minutes. Magnetic properties were measured by a vibrating sample magnetometer and crystalline structures were analyzed by X-ray Diffraction (XRD). Electrical resistivities were measured by a two probe method and compositions of metal ions were measured by X-ray Fluorescence (XRF) analysis.

3. Results and discussions

3.1. X-ray diffraction

Figure 1 shows XRD patterns of samples deposited at various substrate temperatures at a pressure of 1 \times 10^{-4} \text{ Pa} and not annealed after deposition. In the sample deposited at a substrate temperature of room temperature, peaks of Mn-Zn ferrite were not observed but peaks of Fe$_2$O$_3$ were observed. Peaks of Fe$_2$O$_3$ were not observed at substrate temperatures of 450 °C and 500 °C, while (111) peaks of Mn-Zn ferrite were observed at substrate temperatures of 400 °C or higher. Figure 2 shows XRD patterns of samples deposited at a substrate temperature of room temperature and annealed after deposition at various annealing temperatures at a pressure of 1 \times 10^{-4} \text{ Pa}. With an increase in annealing temperature the peaks of Fe$_2$O$_3$ disappeared, but (311) peaks of Mn-Zn ferrite were observed at annealing temperatures of 350 °C or higher. Figure 3 shows XRD patterns of samples deposited at a substrate temperature of room temperature and annealed after deposition at various annealing temperatures in an air atmosphere. Peaks of Fe$_2$O$_3$ were observed at annealing temperatures between 350 to 500 °C and (111) peaks of Mn-Zn ferrite were observed at 400 °C or higher.

Mn-Zn ferrite is generally expressed by the formula MFe$_2$O$_4$. The amount of oxygen per cation needed for the formation of MFe$_2$O$_4$ and Fe$_2$O$_3$ is 1.33 and 1.5, respectively. In the samples deposited at various substrate temperatures at a pressure of 1 \times 10^{-4} \text{ Pa} and samples annealed after deposition at various annealing temperatures at a pressure of 1 \times 10^{-4} \text{ Pa}, oxygen was not provided during heating samples. With an increase in annealing temperature Fe$_2$O$_3$ was less crystallized than MFe$_2$O$_4$ because Fe$_2$O$_3$ needs more oxygen than MFe$_2$O$_4$. On the other hand, in samples annealed after deposition at various annealing temperature in an air atmosphere, oxygen was provided during annealing. So with an increase in annealing temperature MFe$_2$O$_4$ and Fe$_2$O$_3$ were crystallized.

3.2. Magnetic properties
Figure 4 shows the heating temperature dependence of saturation magnetization ($M_s$) for Mn-Zn ferrite at various heating conditions. For samples deposited at various substrate temperatures at a pressure of $1 \times 10^{-4}$ Pa the sample at the substrate temperature of room temperature and 350 °C showed little $M_s$. Magnetization appeared at a substrate temperature of 400 °C or higher and the sample deposited at a substrate temperature of 450 °C had the maximum $M_s$ of 0.34 T. For samples annealed after deposition at a pressure of $1 \times 10^{-4}$ Pa, magnetization appeared at the annealing temperature of 350 °C or higher. The sample annealed at 450 °C had the maximum $M_s$ of 0.58 T. For samples annealed after deposition in an air atmosphere, magnetization appeared at the 400°C or higher and the sample annealed at 400 °C had the maximum $M_s$ of 0.24 T.

From XRD patterns of samples deposited at various substrate temperatures at a pressure of $1 \times 10^{-4}$ Pa, Mn-Zn ferrite crystallization proceeded as the substrate temperature was increased to 450 °C. The Mn-Zn ferrite crystallite degraded with a further increase in the substrate temperature. So $M_s$ of samples deposited at various substrate temperatures at a pressure of $1 \times 10^{-4}$ Pa had a peak value at a substrate temperature of 450 °C. From XRD patterns of samples annealed after deposition at various annealing temperature at a pressure of $1 \times 10^{-4}$ Pa the peak of Fe$_2$O$_3$ is not observed, but (3 1 1) peaks of Mn-Zn ferrite were observed at annealing temperatures of 350 °C or higher, while from XRD patterns of samples annealed after deposition in an air atmosphere peaks of Fe$_2$O$_3$ were observed at annealing temperatures between 350 to 500 °C. Because Mn-Zn ferrite is ferromagnetic and Fe$_2$O$_3$ is nonmagnetic, $M_s$ of samples annealed at a pressure of $1 \times 10^{-4}$ Pa is larger than that of samples annealed after deposition in an air atmosphere. The difference of $M_s$ between samples deposited at various substrate temperatures at a pressure of $1 \times 10^{-4}$ Pa and samples annealed after deposition at various annealing temperature at a pressure of $1 \times 10^{-4}$ Pa is thought to be partly caused by difference of oxygen amount of Mn-Zn ferrites.

3.3 Electric properties
Figure 5 shows the electrical resistivity of Mn-Zn ferrite at various heating conditions. Resistivities of samples deposited at various substrate temperatures at a pressure of $1 \times 10^{-4}$ Pa and samples annealed...
after deposition at various annealing temperature at a pressure of $1 \times 10^{-4}$ Pa decreased with an increase in the heating temperature. The resistivity of samples annealed after deposition in an air atmosphere increased with an increase in the annealing temperature. The resistivity of samples annealed after deposition in an air atmosphere at 450 °C and 500 °C could not be measured because of a measurement limit. They were more than 133 $\Omega \cdot \text{cm}$.

The resistivity of Fe$_2$O$_3$ is high at $\sim 10^6$ $\Omega \cdot \text{cm}$ [3]. The composition of the sample deposited at a substrate temperature of room temperature and not annealed after deposition was Mn$_{10.1}$Zn$_{18.6}$Fe$_{71.1}$O$_x$ in our composition measurement. Because the amount of Fe was more than two times larger than the sum of Mn and Zn, a part of the Fe was replaced by Mn or Zn. As a result the sample consisted of MnZnFe$_2$O$_4$ and FeFe$_2$O$_4$ (Fe$_3$O$_4$). The resistivity of Fe$_3$O$_4$ is very low at $\sim 10^{-3}$ $\Omega \cdot \text{cm}$ which is much lower than that of Fe$_2$O$_3$ [4]. Because the amount of Fe$_2$O$_3$ of the sample annealed after deposition in an air atmosphere increased as described above, the resistivity of the sample annealed after deposition in an air atmosphere increased with an increase in the annealing temperature. On the other hand because the amount of Fe$_2$O$_3$ in the sample annealed after deposition at a pressure of $1 \times 10^{-4}$ Pa decreased, the resistivity of the sample decreased as the annealing temperature increased.

![Figure 5](image_url)

**Figure 5.** The heating temperature dependence of resistivity. The closed squares denote samples deposited at various substrate temperatures at a pressure of $1 \times 10^{-4}$ Pa. The open squares denote samples annealed at various annealing temperature at a pressure of $1 \times 10^{-4}$ Pa after deposition. The open triangles denote samples annealed at various annealing temperature in an air atmosphere after deposition.

4. Conclusions

Basic properties of Mn-Zn ferrite thin films that were fabricated by pulsed laser deposition were evaluated to investigate their possible application as new magnetic cores in thermally assisted magnetic recording. It was found that $M_s$ and the resistivity of Mn-Zn ferrites depend on the amount of oxygen in the annealing atmosphere. A higher $M_s$ of 0.58 T and a lower resistivity of 0.05 $\Omega \cdot \text{cm}$ were obtained for samples annealed after deposition at a pressure of $1 \times 10^{-4}$ Pa and a relatively lower $M_s$ of 0.24 T and a higher resistivity of 60 $\Omega \cdot \text{cm}$ were obtained for samples annealed after deposition in an air atmosphere. These results indicate that Mn-Zn ferrites with a sufficiently high $M_s$ (0.3 T) and a sufficiently high resistivity ($10^2 \Omega \cdot \text{cm}$) can be obtained by controlling the partial pressure of oxygen in the annealing atmosphere. They may thus be used as practical magnetic core materials in a thermally assisted magnetic recording system.

References

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