Effect of Composition and Crystallinity of Epitaxial Ni–Zn Ferrite Films by Pulsed Laser Deposition on their Magnetic Properties

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PLD 法により作製した Ni–Zn フェライト薄膜の磁気特性に及ぼす組成、結晶性の影響

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Epitaxial (Ni–Zn)Fe₂O₄ thin film was prepared on Si(001) substrates using (MgO–Al₂O₃)/CeO₂/YSZ triple buffer layer. In this work, to increase remanent magnetization (M_r) and decrease coercive field (H_c), for epitaxial (Ni–Zn)Fe₂O₄ thin film, the effect of substrate temperature, oxygen pressure and composition on the magnetic properties was examined. It was clarified that the remanent magnetization and coercive field were strongly influenced by temperature and oxygen pressure. In order to obtain high M_r and low H_c , it was thought that a substrate temperature of 800°C and oxygen pressure 1.3 Pa were optimal conditions. As regarding the composition, M_r could be obtained to a maximum of 3.96×10^{-1} Wb/m² by changing the quantity of Zn and Fe ($M_s = 5.31 \times 10^{-1}$ Wb/m², $H_c = 1.35 \times 10^1$ kA/m).

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1. Introduction

Recently, researches for field effect transistor (FET)-type ferroelectric random access memory (FRAM) has been extensively carried out. We are considering a possibility that FRAM performance would be modified using ferromagnetic layer.¹⁾ To achieve the new memory, the control of the electric current by using Hall effect is the most important and thus ferrite having large remanent magnetization is selected as the ferromagnetic layer. Moreover to achieve maximum performance, heteroepitaxial ferroelectric/ferromagnetic/semiconductor structure is required. Ferroelectric/ferromagnetic heterostructures on Si are first proposed by Wakiya et al.¹⁾ They prepared heteroepitaxial NiFe₂O₄ thin film on Si(001) substrate via (5.3 mol% Al₂O₃ doped-MgO)/CeO₂/YSZ buffer layers.²⁾ However, the remanent magnetization (M_r) of NiFe₂O₄ was small and H_c value was large. Therefore, to increase M_r and decrease H_c , preparation of heteroepitaxial (Ni–Zn)Fe₂O₄ on Si(001) substrate was required. To achieve epitaxial (Ni–Zn)Fe₂O₄ thin film, some buffer layers for NiFe₂O₄ thin film were used.

The magnetization of Mn–Zn ferrite, Ni–Zn ferrite has been reported.^{3)–8)} However there are a few researches, which are optimizing substrate temperature, oxygen pressure, and composition in order to acquire the good magnetic characteristic (high M_r , low H_c). Furthermore, the relation of crystalline and the magnetic characteristic has not been clarified yet. In this paper, to improve the soft magnetic properties (M_r , H_c) of the (Ni–Zn)Fe₂O₄ thin films, we describe the effect of crystallization on the magnetic properties of (Ni–Zn)Fe₂O₄ thin films at various substrate temperatures and O₂ pressures, and the effect of composition on the magnetic properties of (Ni–Zn)Fe₂O₄ thin films at constant growth conditions.

2. Experimental

2.1 Film preparation and characteristic measurement

All thin films were deposited on Si(001) by pulsed laser deposition with a KrF excimer laser ($\lambda = 248$ nm). The laser beam was focused on the target by at an angle of 45°

Table 1. Deposition Conditions of Ni–Zn Ferrite Thin Film

Laser	KrF excimer laser ($\lambda = 248$ nm)
Target	YSZ(8Y), CeO ₂ , MgO–Al ₂ O ₃ (5.3 mol% Al ₂ O ₃), Ni _x Zn _y Fe _{3-x-y} O ₄ (0 < x, y < 1.5) ceramic disks
Target–Substrate distance	55 mm
Repetition rate	7 Hz
Spot size	0.1 cm ²
Laser energy density	2.0 J/cm ²
Film thickness	YSZ:10 nm, CeO ₂ :18 nm, MgO–Al ₂ O ₃ :3 nm, (Ni–Zn)Fe ₂ O ₄ :150 nm
Substrate temperature	YSZ, CeO ₂ , MgO–Al ₂ O ₃ : 800 °C, 650~800 °C
Oxygen pressure	YSZ, CeO ₂ , MgO–Al ₂ O ₃ : 7.3×10^{-2} Pa, (Ni–Zn)Fe ₂ O ₄ : $1.3 \times 10^{-3} \sim 1.3 \times 10^1$ Pa

and with a spot size of 0.1 cm². The laser energy density was about 2 J/cm² per pulse, and the laser repetition rate was 7 Hz. The target was kept at a distance of 55 mm from the substrate and rotated continuously during deposition. The substrates were heated to 800°C at a base pressure of $< 1.3 \times 10^{-4}$ Pa. The typical deposition conditions for PLD were shown in Table 1.

The structural properties of the films were characterized by X-ray diffraction (XRD) using Cu K α radiation operating at 40 kV–40 mA (X'Pert-MPD(θ – θ , Open Eulerian Cradle), Phillips). The composition of the films was analyzed using an X-ray fluorescent spectroscopy (XRF) (wavelength dispersive spectroscopy (WDS), (PW2404, Phillips, Netherlands)). The magnetization M_s , M_r and the coercive field H_c were measured in the plane of the film using a vibrating sample magnetometry (VSM).

2.2 Deficiency of Zn in the films as compared with the targets

It is well known that the MnZn–ferrite, NiZn–ferrite films

Fig. 1. Decrease in Zn concentration(%) vs O_2 gas pressure at 650, 800°C.

Fig. 2. Effect on the magnetization of epitaxial growth.

were deficient in Zn as compared to the ferrite targets.³⁾⁻⁷⁾

Figure 1 shows a deficiency of Zn in the films as a function of substrate temperature and oxygen pressure to prepare for the films with the constant Ni, Zn and Fe concentrations irrespective of the deposition conditions. Zn concentration is decreased with decrease in oxygen pressure at 800°C, although the data suggest a slight deficiency of Zn at 650°C as compared with the original targets. Therefore in order to compensate for the Zn deficiency in the films, these targets were prepared with excess Zn content.

3. Results and discussion

3.1 Heteroepitaxial (Ni-Zn)Fe₂O₄ thin films

In this work, all $Ni_xZn_yFe_{3-x-y}O_4$ ($0 \leq x, y \leq 0.9$)/5.3 mol% Al_2O_3 doped-MgO/CeO₂/YSZ thin films prepared at various substrate temperature (650–800°C) and O_2 pressure (1.3×10^{-4} – 1.3×10^{-3} Pa) conditions were grown heteroepitaxially on Si(001).

Figure 2 and Table 2 show the magnetic properties of heteroepitaxial and polycrystalline Ni-Zn ferrite films ($Ni_{0.42}Zn_{0.56}Fe_{2.02}O_4$) deposited at the same conditions (800°C, 1.3 Pa). The coercive field H_c , the saturation mag-

Table 2. Magnetizations for Epitaxial and Polycrystalline Films

	M_s (Wb/m ²)	M_r (Wb/m ²)	H_c (kA/m)
Epitaxial film	5.10×10^{-1}	2.51×10^{-1}	8.75
Polycrystalline film	5.04×10^{-1}	1.88×10^{-1}	8.43

Fig. 3. Comparison of M_s , M_r , and H_c for $Ni_{0.4}Zn_{0.6}Fe_2O_4$ films as O_2 pressure of 7.3×10^{-2} Pa at 650, 700, 750 and 800°C.

Fig. 4. Comparison of M_s , M_r , and H_c for $Ni_{0.4}Zn_{0.6}Fe_2O_4$ films as a function of oxygen pressure.

netization M_s of the heteroepitaxial film were very close to the values for polycrystalline film. The remanent magnetization M_r , on the other hand, was larger than those of the polycrystalline film. This indicates that M_r is strongly influenced by the heteroepitaxial growth.⁸⁾

3.2 The magnetic and crystalline properties as functions of substrate temperature and O_2 pressure

Figures 3 and 4 show M_s , M_r and H_c as a function of substrate temperature at O_2 pressure of 7.3×10^{-2} Pa, and O_2 pressure at 800°C of substrate temperature, respectively. Generally in composition of Ni-Zn ferrite, there are many researches currently studied at a rate of Ni:Zn:Fe = 13.3:20:66.7.^{5),7)} Then, it adjusted so that the composition might be set to $Ni_{0.4}Zn_{0.6}Fe_2O_4$ in each substrate temperature and oxygen pressure. H_c decreased and M_s , M_r , on the other

Fig. 5. Change of Ni-Zn ferrite(400) FWHM and axial ratio of a/c with temperature.

Fig. 6. Relationship between oxygen pressure and FWHM, axial ratio of a/c .

hand, increased with increasing substrate temperature (Fig. 3). Figure 4 shows H_c decreased with increasing O_2 pressure, M_r increased with O_2 pressure and reached a maximum at about 1.3 Pa, then decreased. However, about $2.76 \times 10^{-1} \text{ Wb/m}^2$ was shown in every O_2 pressure about M_s while H_c and M_r were influenced of O_2 pressure.

Figures 5 and 6 show the change of the ω -rocking curve full-width at half maxima (FWHM) for the $Ni_{0.4}Zn_{0.6}Fe_2O_4$ (400) peak and axial ratio of c/a as functions of substrate temperature and O_2 pressure. The following was considered from these figures, the FWHM value decreased with increasing substrate temperature and ca 1.8 at about 1.3 Pa, c/a increased and approached 1 with increasing substrate temperature and O_2 pressure. The relation of H_c and temperature is similar to the relation between c/a and substrate temperature, oxygen pressure, and moreover, M_r is similar to the relation of FWHM and these. As substrate temperature is increased, the atomic mobility is enhanced,^{(4)–(6)} the tilting of the grain boundaries is decreased, and with increasing O_2 pressure, the influence by the oxygen defect decreases, the strains are relieved. Consequently, it resulted to reduction in H_c . With increasing substrate temperature, and at the reach of 1.3 Pa, the crystalline is improved, and M_r increases.

Fig. 7. M_r , M_s , and H_c vs Zn^{2+} ion concentrations of $Ni_{0.85-x}Zn_xFe_{2.15}O_4$.

Fig. 8. M_s , M_r , and H_c vs Fe concentration of $Ni_xZn_yFe_{3-x-y}O_4$ ($x:y=40:60$).

3.3 The magnetic properties as a function of composition

Figure 7 shows the correlation between the magnetic properties and the Zn concentration of $Ni_{0.85-x}Zn_xFe_{2.15}O_4$ on at substrate temperature of 800°C, O_2 pressure of 1.3 Pa. Although M_s and M_r become large with the increase in the amount of Zn to (Ni + Zn), they become small if the amount of Zn to (Ni + Zn) exceeds 65%. About H_c , it becomes small monotonously with the increase in the amount of Zn to (Ni + Zn).

The magnetization of the spinel depends on the exchange interaction between oppositely polarized magnetic ions on the tetrahedral-A and octahedral-B sites of the spinel structure.⁽⁶⁾ It is well known that small increases in the Zn concentration of a spinel of the type $Me_{1-x}Zn_xFe_2O_4$ (Me: metal cation) may enhance the magnetization due to a dilution of the Fe^{3+} ions on the A sites. However, the magnetic ions of A site may be small, the exchange interaction between A-B may become weak and also even the ferro coupling may disappears by the exchange interaction between other ions if the amount of Zn becomes superfluous. Consequently, it is thought that magnetization became

Fig. 9. Magnetic properties of $\text{Ni}_x\text{Zn}_y\text{Fe}_{3-x-y}\text{O}_4$ as a function of composition.

small. Therefore, it turns out that we can get high magnetization by making the amount of Zn to (Ni+Zn) into 50–65%.

M_s , M_r , and H_c as a function of Fe concentrations of $\text{Ni}_x\text{Zn}_y\text{Fe}_{3-x-y}\text{O}_4$ ($x:y=40:60$) are shown in Fig. 8. In this figure, with the increase in the amount of Fe, M_s , M_r , and H_c become large. The reason can be explained from the following things. There is an excess number of Fe^{2+} ions on the B site, and in a magnetic moment, they are $\text{Fe}^{2+} > \text{Ni}^{2+}$, Zn^{2+} . That is, since the whole amount of magnetic moments becomes large because the quantity of Fe increases, it is thought that M_r and M_s also became large. Moreover, when Fe is made superfluous, diffusion of Fe^{2+} through a positive ion lattice vacancy under crystal becomes easy to take place like $\text{Fe}^{3+} + e^- \rightleftharpoons \text{Fe}^{2+}$, and it is thought that the induced

magnetic anisotropy increases. That was connected to the increase in H_c . As a conclusion of composition, the relation between Zn, Fe content, and the magnetic characteristic is shown in Fig. 9.

4. Conclusions

Heteroepitaxial $(\text{Ni-Zn})\text{Fe}_2\text{O}_4$ thin films on Si(100) substrate via (5.3 mol% Al_2O_3 doped-MgO)/ CeO_2 /YSZ buffer layers have been obtained by PLD on Si (100) substrate at various substrate temperature and O_2 pressure conditions, from targets prepared by various compositions. We have examined the magnetic and crystalline properties to improve the soft magnetic properties (M_r , H_c) of the $(\text{Ni-Zn})\text{Fe}_2\text{O}_4$ thin films. This investigation shows that H_c and M_r are strongly influenced by the crystalline of the films, and M_s , M_r , and H_c depend more on the composition. It turns out as conditions for obtaining optimal M_r and H_c that they are the substrate temperature of 800°C , and O_2 pressure of 1.3 Pa. The magnetic properties as a function of composition. It is very likely that the changes in the M_s , M_r and H_c of the films could be due to the presence of Zn^{2+} , Fe^{2+} , Fe^{3+} ions.

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