

Preparation of High Resistive and Low Coercive Force Magnetite Films by Chemical Reaction from an Aqueous Solution

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A magnetite (Fe_3O_4) film containing small amount of Zn element has been fabricated onto a ZnO covered glass substrate by immersing into an aqueous solution containing an iron (III) nitrate hydrous and DMAB at 323 K. The magnetite film containing Zn showed magnetic property of 380 emu/cc in saturation magnetization and 40 Oe in coercive force, and very high resistivity of $5.7 \times 10^6 \Omega\text{cm}$.

1.Introduction

Magnetite (Fe_3O_4) and ferrite (MFe_2O_4 ; $\text{M} = \text{Zn}, \text{Ni}$) films have been used in several applications such as a magnetic recording medium, microwave device, and conformity living body materials of chemical-medical fields because of their electrical and magnetic characteristics. These films are prepared by several gas-phase deposition techniques such as chemical vapor deposition (CVD), molecular beam epitaxy (MBE), magnetron sputtering method, and laser ablation techniques, and are not appropriate to the industrial uses because of high preparation cost and difficulties of the preparation.

A preparation of the oxide films from aqueous solutions has attracted increasing attention as the preparation technique, and has several advantages over the gas-phase deposition techniques because of less hazardous, more environmentally friendly, low cost.

We have proposed chemical solution process using a nitrate-reduction reaction in an aqueous solution and demonstrated preparations of zinc oxide, indium

oxide, cerium dioxide, and magnetite (Fe_3O_4) by using the chemical solution process.¹⁻³ The magnetite film showed characteristic magnetic properties of 480 emu/cc in saturation magnetization and 150 Oe in coercive force and extremely high resistivity of $1.5 \times 10^3 \Omega\text{cm}$ which was much higher by about six orders in magnitude than that for bulk Fe_3O_4 . Although the magnetite film is a candidate as a high-frequency magnetic interference shielding material, further decrease in coercive force and increase in resistivity are indispensable for the industrial use. Here, we found a magnetite film containing small amount of zinc prepared by chemical solution process showed unique magnetic characteristics appropriated to the magnetic shielding material. In this study, we prepared the Zn contained magnetite film by the chemical reactions onto ZnO coated glass substrate and the structural, magnetic, and electric characterization were carried out

2.Experimental procedure

0.15 μm -thick ZnO coated glass substrates were prepared by immersing glass substrate (Corning #1737) into an aqueous solution containing 0.1 mol/l zinc nitrate hydrous and 0.03 mol/l dimethylamineborane (DMAB) at 343 K for two hours. The solution showed pH value of 6.0. Prior to deposition, the glass substrates were rinsed in acetone and then catalyzed using an industrially employed three-step activation process (C. Uyemura & Co., Ltd., S-10X, MSA-27 and A-10X).

1 μm -thick Zn-contained magnetite films were deposited onto the ZnO coated glass substrates by immersing a substrate for two hours in an aqueous solution containing 0.0125 mol/l iron (III) nitrate hydrous and 0.03 mol/l DMAB at 323 K. The solution showed pH value of 4.0.

3. Results and discussion

Fig. 1 shows depth profiles of Fe, O, Zn, and B signals for the film by detecting Fe2p, O1s, B1s, and Zn2p electron spectra. The profiles were taken with an ESCA. The intensities of Fe, Zn, O, and B signals were almost constant at sputtering time up to 80 min, and then the intensity of Fe signal decreased and the intensity of Zn signal increased with increase in sputtering time above 100 min. Since the Zn element incorporated in the black film was not contained in the preparation solution, the Zn element was originated from the under ZnO layer in substrate. And, the B element was originated from the DMAB containing in the preparation solution as reported for ZnO film.

The electron of Fe2p, ZnLMM, O1s, and B1s spectra were almost the same in profile and peak energies regardless of sputtering times up to 100 minutes. The Fe2p spectrum showed a peak at 709.7 eV, which was closed to that of Fe2p_{3/2} peak eV for Fe₃O₄. And, a shoulder

could be observed at low energy side of the peak. The Fe2p_{3/2} spectrum could be deconvoluted using a least-square curve fitting method with a mixture of Gaussian and Lorentzian functions on a Shirley -type background.⁴ Four components including Fe²⁺ (708.7 eV) and Fe³⁺ components (710.9 eV) could be observed on the deconvolution result. And, a component observed at 707 eV could be identified as Fe2p_{3/2} peak in metallic Fe. The intensity ratio of three states was estimated to be 48, 45, and 7 for Fe³⁺, Fe²⁺, and Fe⁰ states, indicating that the film was in a condition far away from the equilibrium state. The Zn LMM spectrum showed a peak at 271.4 eV, which was attributed to Zn²⁺ state for ZnO. The peak energy of O1s peak was 529.7 eV, which was close to that for O²⁻ state ZnO (530.4 eV) and Fe₃O₄ (530.0 eV). The weak peak of B1s was observed at the energy of 191.0 eV, which corresponded to B³⁺ state for B₂O₃. The composition ratio after 2 minutes sputtering was calculated from relative sensitivity coefficient and peak area and the film contained 40 mol% Fe, 2.3 mol% Zn, 0.9 mol% B, and 56.4 mol% O.

Fig. 2 shows X-ray diffraction spectra for ZnO

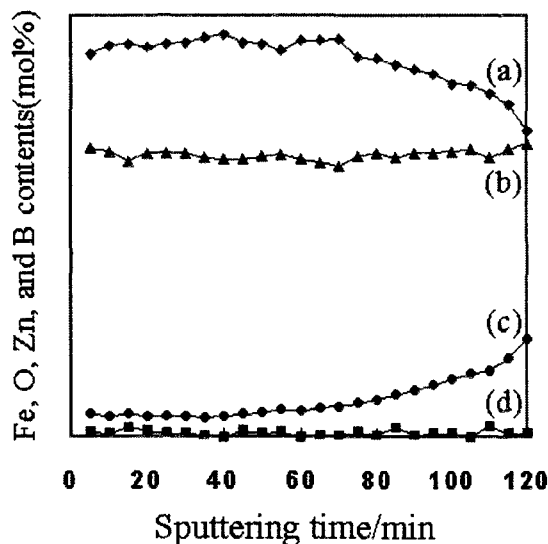


Fig. 1 Depth profiles of Fe(a), O(b), Zn(c), and B(d) signals of Fe₃O₄ films prepared onto the ZnO layer.

coated glass substrate before and after of the deposition Zn-contained magnetite film. The ZnO coated glass substrate showed a broadened peak originated from the glass substrate with amorphous structure and sharp peaks assigned to those of ZnO with a wurtzite structure. The strong (002) diffracted line indicated that the ZnO film had a (001) preferred orientation. All the diffraction peaks for Zn contained magnetite film seen in Fig.2(b) were assigned to those of Fe_3O_4 with a spinel cubic structure. Any peaks identified to metallic Fe, boron and zinc compounds could not be seen on the spectra. The Zn contained magnetite film had random orientation, since the relative intensities of the diffracted X-ray lines almost resembled those tabulated in ICDD card. The unit-cell parameter of Zn contained magnetite film calculated from the peak angles was 0.8375 nm, which was smaller than those for Fe_3O_4 and ZnFe_2O_4 . These facts suggested that the Zn contained magnetite film had a spinel cubic lattice with an atomic arrangement deferent to that for conventional ZnFe_2O_4 .

The ZnO film in substrate was somewhat dissolved into the solution containing Fe-nitrate and DMAB with pH value of 4.0, where Zn^{2+} state is more in the potential-pH diagram.⁵ And, during the deposition of Fe_3O_4 , the dissolved Zn element was incorporated into the

film, resulting in the formation of Zn contained magnetite film.

Fig. 3 shows magnetization curves for ZnO coated substrate before and after the formation of Zn contained magnetite film. The ZnO coated glass substrate exhibited anti-ferromagnetic feature. Zn incorporated Fe_3O_4 film exhibited ferromagnetic with saturation magnetization of 380 emu/cc, and coercive force of 40 Oe. The saturation magnetization is slightly smaller than 480 emu/cc of Fe_3O_4 prepared on glass substrate due to incorporation of Zn element. The coercive force was smaller than these (150 Oe) of bulk Fe_3O_4 and Fe_3O_4 prepared on glass substrate. This will be attributed to the incorporated Zn element and change in structural characteristics.

The Zn contained magnetite film showed a sheet resistivity of $6.9 \times 10^{10} \Omega$ and the resistivity calculated from the sheet resistivity and thickness of film was $5.7 \times 10^6 \Omega\text{cm}$. The resistivity is much higher by about nine orders in magnitude than that of bulk Fe_3O_4 and by three orders in magnitude than that of chemically deposited magnetite film. This will be attributed to the incorporated B^{3+} and Zn^{2+} ions into spinel cubic structure.

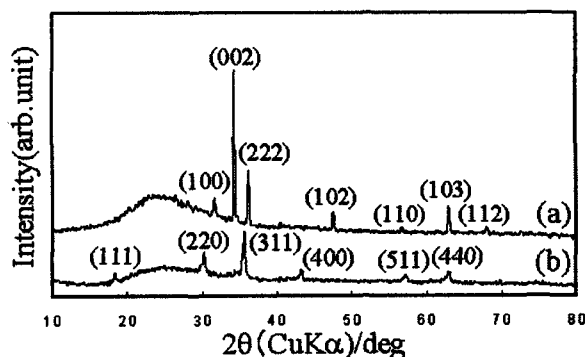


Fig. 2 X-ray diffraction patterns of ZnO (a), Fe_3O_4 (b) films prepared by chemical deposition onto #1737 glass.

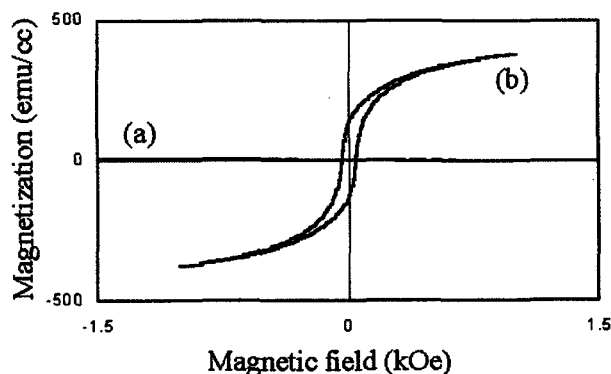


Fig. 3 Magnetization curves for ZnO (a), Fe_3O_4 (b) films prepared onto #1737 glass.

Conclusion - A Zn contained magnetite (Fe_3O_4) film with a spinel cubic structure has been prepared onto a substrate covered with ZnO film by immersing into an aqueous solution containing an iron (III) nitrate hydrous and DMAB at 323 K. The film showed magnetic property of 380 emu/cc in saturation magnetization and 40 Oe in coercive force and very high resistivity of $5.7 \times 10^6 \Omega\text{cm}$.

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