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Chemical vapour deposition of epitaxial Ni–Zn ferrite films by thermal decomposition of acetylacetonato complexes

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Epitaxial (Ni, Zn)Fe_2O_4 films were prepared on (1 0 0) MgO single crystal substrate by low-pressure chemical vapour deposition using a thermal decomposition of acetylacetonatocomplexes, $Ni(acac)_2$, $Zn(acac)_2$ and $Fe(acac)_3$. These complexes were evaporated at 157, 79 and 146° C, respectively, and transported with nitrogen carrier gas (flow rate 100 ml min^{-1}) to the deposition furnace. Polycrystalline and epitaxial films were grown at 500 to 600 and 600 to 650° C, respectively, under a pressure of 12 torr. The epitaxial film of $Ni_{1-x}Zn_xFe_2O_4$ ($x \simeq 0.4$) treated at 600° C for 60 min, showed the saturation magnetization of 67 e.m.u. g^{-1} and the coercive force of 20 to 30 Oe.

1. Introduction

Preparation of nickel and Ni–Zn ferrite films by thermal decomposition of metal acetylacetonates was reported previously [1], in which three kinds of acetylacetonatocomplexes, $Ni(acac)_2$, $Zn(acac)_2$ and $Fe(acac)_3$ were used as the starting vapour source. As-grown films deposited at the substrate temperature of 330 to 550° C under a pressure of 1 atm, however, were amorphous or slightly crystalline, so that it was necessary to heat-treat these films at higher temperatures (800 to 1000° C) in order to increase the crystallinity of ferrite films and to improve the magnetic properties.

In the present paper, epitaxial films of Ni–Zn ferrite formulated briefly as (Ni, Zn)Fe_2O_4 were grown directly on periclase single crystal (MgO) by a low-pressure chemical vapour deposition (CVD) using thermal decomposition of acetylacetonatocomplexes. Growth conditions of (Ni, Zn)Fe_2O_4 films and some magnetic properties for the application to soft ferrite thin films [2, 3] were investigated by means of a similar experimental technique to that used on the Mn–Zn ferrite films [4, 5].

2. Experimental procedure

Fig. 1 shows a schematic drawing (a plane figure) of the CVD reactor for growing Ni–Zn ferrite films. Three kinds of commercially available acetylacetonatocomplexes, $Ni(acac)_2 \cdot 2H_2O$, $Zn(acac)_2 \cdot 2H_2O$ and $Fe(acac)_3$, were charged in quartz boats (80 to 100 mg for each boat), which were heated independently in different evaporation furnaces. The hydrated water dissociates in the early stage of heating at 70 to 80° C [4]. Nitrogen gas (flow rate 100 ml min^{-1}) as a carrier gas for each complex was streamed into the furnace, from which the evaporated complexes were mixed at the branched tube and transported to the deposition furnace. The temperature of the branched tube was held at 160° C to prevent the condensation of the mixed vapour. The inlet part of the deposition furnace was cooled by a water cooling pipe to make a steep temperature gradient between the branched tube and the deposition zone. Silica glass or cleaved (1 0 0) MgO single crystal substrate (10 mm × 10 mm) was heated at the centre of the deposition furnace in the temperature range 400 to 800° C. Oxygen gas (flow rate 5 to 30 ml min^{-1}) was introduced directly to 5 to 10 cm ahead of the substrate by a thin quartz pipe. The pressure in the evaporation furnaces and the deposition furnace was kept constant at 12 torr.

The films grown were characterized by X-ray diffraction, scanning electron microscope (SEM) and reflection high-energy electron diffraction (RHEED). The magnetic properties were evaluated by a vibrating sample magnetometer (VSM) and a magnetic balance.

3. Results and discussion

3.1. Growth conditions of single-phase $NiFe_2O_4$ films

Optimum growth conditions of single-phase nickel ferrite ($NiFe_2O_4$) films were determined as a basic approach to the preparation of Ni–Zn ferrite films. Fig. 2 shows the relationship between the saturation magnetization (σ_s) of $NiFe_2O_4$ films obtained on a silica glass substrate and the deposition temperature (T_d), where the treatment time was kept constant at 20 min. No $Zn(acac)_2 \cdot 2H_2O$ was charged in the evaporation furnace [2] of the nickel complex in Fig. 1, but nitrogen carrier gas (flow rate 100 ml min^{-1}) only was streamed. In order to obtain single-phase $NiFe_2O_4$, the evaporation temperatures of $Ni(acac)_2$ and $Fe(acac)_3$ were kept constant at 157 and 146° C,

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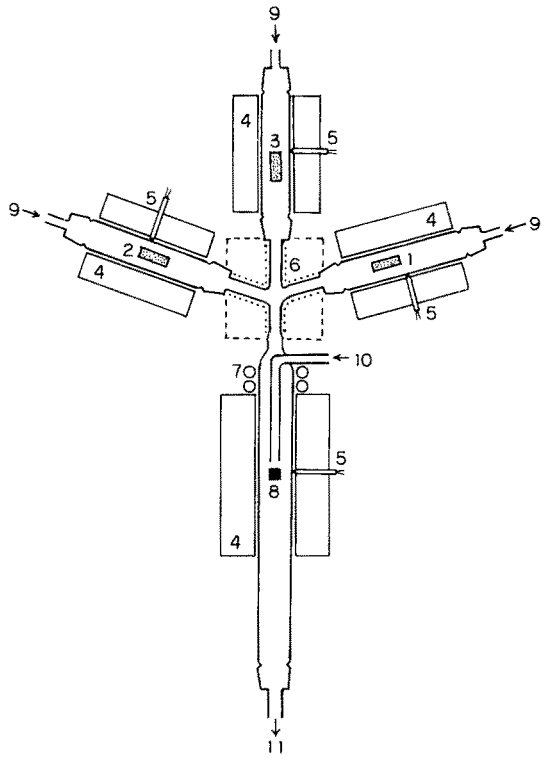

Figure 1 Schematic drawing of the CVD reactor for growing Ni–Zn ferrite films: 1, $Ni(acac)_2 \cdot 2H_2O$; 2, $Zn(acac)_2 \cdot 2H_2O$; 3, $Fe(acac)_3$; 4, electric resistance furnace; 5, thermocouple; 6, nichrome heater; 7, cooling pipe; 8, substrate; 9, N_2; 10, O_2; 11, to rotary pump.

respectively, unless a small amount of α-Fe_2O_3 or NiO was codeposited with $NiFe_2O_4$ corresponding to the excess amount of evaporated iron or nickel complex, respectively [1]. The optimum flow rate of oxygen was 15 ml min^{-1}.

The film deposited at 400 to 450° C was low crystalline $NiFe_2O_4$ and had a σ_s value lower than 30 e.m.u. g^{-1}. The crystallinity and saturation magnetization increased with increasing temperature up to 500° C. The $NiFe_2O_4$ film grown at 500 to 550° C had a highly preferred orientation of the (1 0 0) plane. The lattice constant $a_0 = 0.8339$ nm, the saturation magnetization at room temperature, $\sigma_s = 50$ e.m.u. g^{-1}, and the Curie temperature, $T_c = 590$° C (see Fig. 4), were consistent with the reported values of single-phase and crystalline $NiFe_2O_4$ [6, 7]. At temperatures higher than

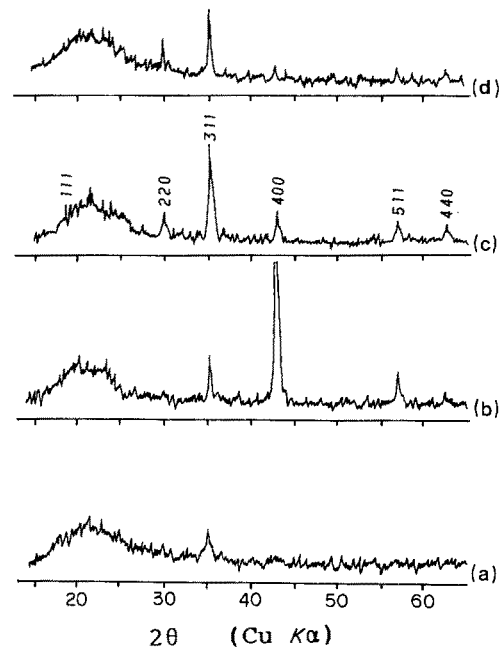

Figure 3 X-ray diffraction patterns of (Ni, Zn)Fe_2O_4 films obtained at various temperatures on silica glass substrate: deposition temperature: (a) 459° C, (b) 550° C, (c) 600° C, (d) 700° C.

600° C, isotropic $NiFe_2O_4$ films were obtained with the σ_s value decreasing slightly as the temperature increased. The film thickness decreased above 700° C due to the powder formation of $NiFe_2O_4$ by a homogeneous nucleation in the vapour phase.

3.2. Growth conditions of polycrystalline Ni–Zn ferrite films

Polycrystalline (Ni, Zn)Fe_2O_4 films were prepared on silica glass substrates, when $Ni(acac)_2$, $Zn(acac)_2$ and $Fe(acac)_3$ were evaporated at 157, 79 and 146° C, respectively [1]. The temperature dependence of crystallinity, preferred orientation and saturation magnetization showed an analogous tendency to those of $NiFe_2O_4$ as described in Section 3.1. Fig. 3 shows the variation of X-ray diffraction patterns with deposition temperature. A halo pattern near $2\theta = 22°$ corresponds to the reflection from amorphous silica glass substrate. The film deposited at 450° C was low crystalline. The

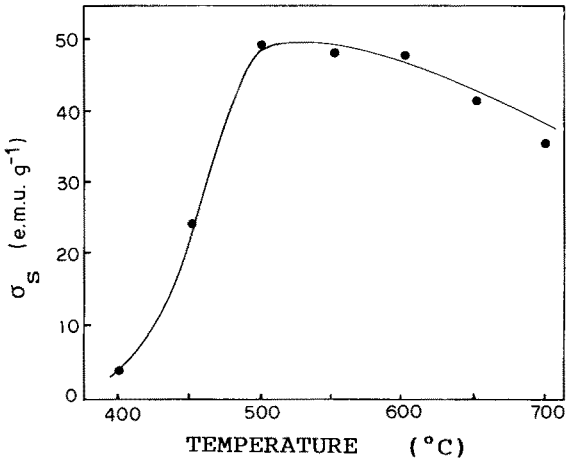

Figure 2 Saturation magnetization (σ_s) of $NiFe_2O_4$ films on silica glass plotted against deposition temperature (T_d): treatment time = 20 min.

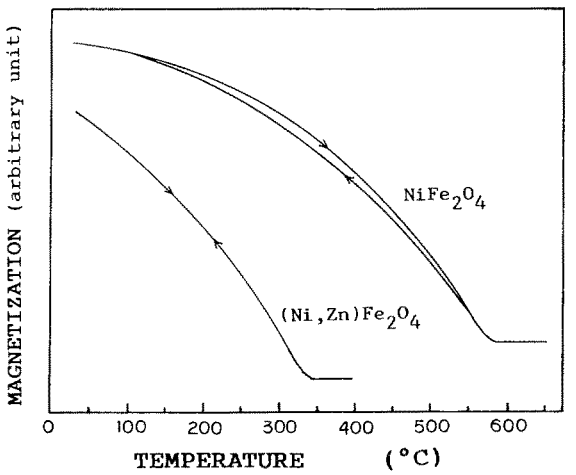

Figure 4 Thermomagnetic curves of $NiFe_2O_4$ and (Ni, Zn)Fe_2O_4 films: deposition temperature = 600° C.

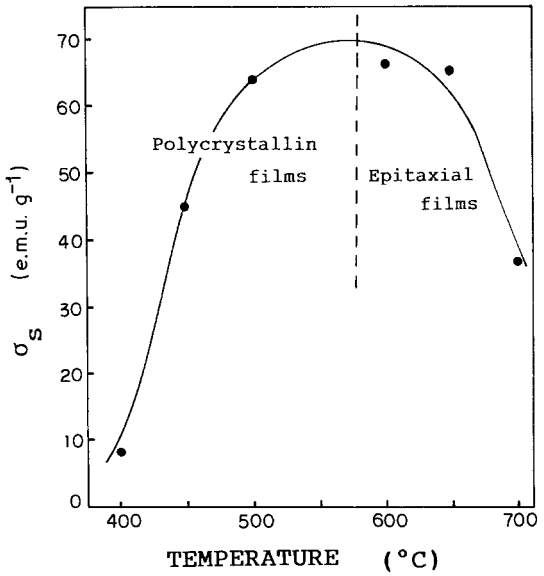

Figure 5 Saturation magnetization (σ_s) of (Ni, Zn)Fe_2O_4 films on MgO single crystal plotted against deposition temperature (T_d): treatment time = 20 min.

(Ni, Zn)Fe_2O_4 film having a highly preferred orientation of the (1 0 0) plane was obtained at 550° C (see Fig. 3b) when the σ_s value was 62 e.m.u. g^{-1} and the coercive force, H_c, was 50 to 100 Oe. Isotropic $NiFe_2O_4$ film was prepared at temperatures higher than 600° C when the σ_s value decreased to less than 55 e.m.u. g^{-1} with deposition temperature.

Fig. 4 shows the thermomagnetic curves of $NiFe_2O_4$ and (Ni, Zn)Fe_2O_4 films prepared on silica glass substrates at 600° C. The Curie temperatures were 590 and 340° C, respectively. It is confirmed from these typical thermomagnetic curves for spinel-type ferrites that the solid solution (Ni, Zn)Fe_2O_4 between $NiFe_2O_4$ and $ZnFe_2O_4$ is formed. The value of x in $Ni_{1-x}Zn_xFe_2O_4$ is evaluated to be about 0.4, from the measurements of the Curie temperature and the lattice constant (a_0 = 0.8399 nm).

3.3. Preparation and magnetic properties of epitaxial Ni–Zn ferrite films

Epitaxial growth conditions of (Ni, Zn)Fe_2O_4 films were investigated using (1 0 0) MgO single crystal as substrate. Because the misfit of the lattice constant of (Ni, Zn)Fe_2O_4 (a_0 = 0.8399 nm) to MgO ($2a_0$ = 0.8426 nm) is 0.32%, there is a high possibility of growing an epitaxial film of (Ni, Zn)Fe_2O_4. The evaporation conditions of the metal complexes were the same as those in Section 3.2. Fig. 5 shows the saturation magnetization (σ_s) as a function of deposition temperature (T_d). The increase in the σ_s value up to T_d = 500° C is an analogous tendency to the polycrystalline (Ni, Zn)Fe_2O_4 films prepared on silica glass substrates. The film grown on (1 0 0) MgO at T_d = 550° C was still a polycrystalline (Ni, Zn)Fe_2O_4 which has a strong preferred orientation of the (1 0 0) plane. In the temperature range T_d = 600 to 650° C, however, an epitaxial film of (Ni, Zn)Fe_2O_4 was grown. Fig. 6 shows the RHEED patterns of the polycrystalline and epitaxial films of (Ni, Zn)Fe_2O_4 which were grown at 550 and 650° C, respectively, on (1 0 0) MgO single crystal. The epitaxial (Ni, Zn)Fe_2O_4 film obtained at 600° C for 1 h, had a film thickness of about 600 nm. The growth rate (10 nm min^{-1}) is a little lower than that (11 to 12 nm min^{-1}) of polycrystalline (Ni, Zn)Fe_2O_4 film. The σ_s value of this film was 67 e.m.u. g^{-1} and the H_c value was 20 to 30 Oe.

TABLE I Comparison between polycrystalline and epitaxial (Ni, Zn)Fe_2O_4 films

	Polycrystalline	Epitaxial
Substrate	silica glass	MgO single crystal
Deposition temperature (° C)	500–600	600–650
Saturation magnetization (e.m.u. g^{-1})	54–62	60–67
Coercive force (Oe)	50–100	20–30

4. Conclusions

Polycrystalline and epitaxial films of (Ni, Zn)Fe_2O_4 were grown on silica glass or MgO single crystal substrates by thermal decomposition CVD of metal acetylacetonates. The growth conditions and magnetic properties of both films are summarized in Table I. Epitaxial (Ni, Zn)Fe_2O_4 film has higher saturation magnetization and lower coercive force, which is more applicable to soft ferrite devices than the polycrystalline film.

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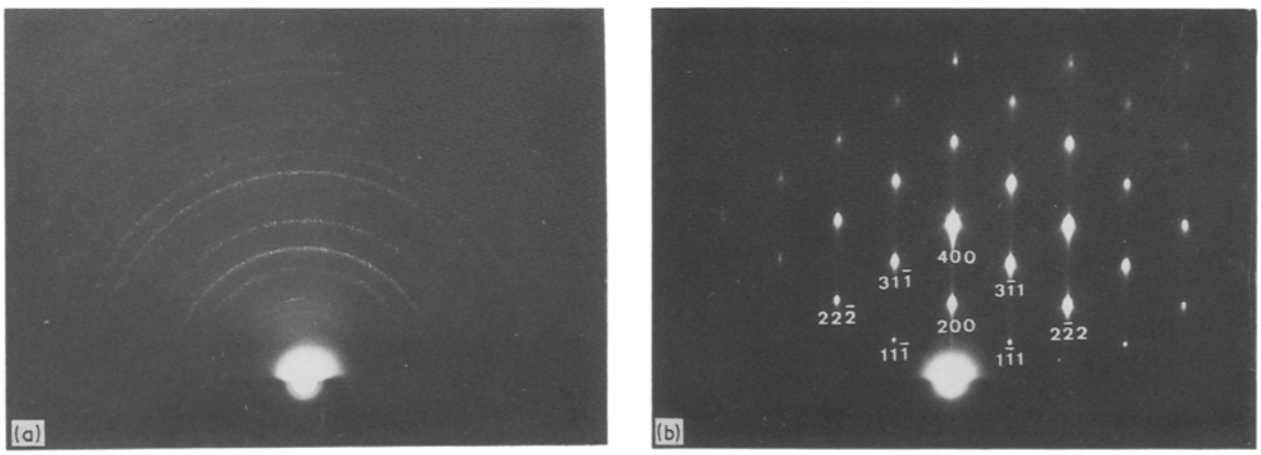

Figure 6 RHEED patterns of polycrystalline (a) and epitaxial (b) films of (Ni, Zn)Fe_2O_4. Substrate, (1 0 0) MgO single crystal; deposition temperature: (a) 550°C, (b) 650° C.

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