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

HIDEAKI ITOH, TOSHIYA UEMURA, HIROFUMI YAMAGUCHI, SHIGEHARU NAKA
Synthetic Crystal Research Laboratory, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

Epitaxial (Ni, Zn)Fe$_2$O$_4$ 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$_x$Fe$_2$O$_4$ (x ≈ 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$_2$O$_4$ 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$_2$O$_4$ 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)$_2$ · 2H$_2$O, Zn(acac)$_2$ · 2H$_2$O 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$_2$O$_4$ films
Optimum growth conditions of single-phase nickel ferrite (NiFe$_2$O$_4$) films were determined as a basic approach to the preparation of Ni–Zn ferrite films. Fig. 2 shows the relationship between the saturation magnetization ($\mu_t$) of NiFe$_2$O$_4$ 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)$_2$ · 2H$_2$O 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$_2$O$_4$, the evaporation temperatures of Ni(acac)$_2$ and Fe(acac)$_3$ were kept constant at 157 and 146°C.
respectively, unless a small amount of $\alpha$-Fe$_2$O$_3$ or NiO was codeposited with NiFe$_2$O$_4$ 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$_2$O$_4$ and had a $\sigma_r$ value lower than 30 e.m.u. g$^{-1}$. The crystallinity and saturation magnetization increased with increasing temperature up to 500°C. The NiFe$_2$O$_4$ film grown at 500 to 550°C had a highly preferred orientation of the (100) plane. The lattice constant $a_0 = 0.8339$ nm, the saturation magnetization at room temperature, $\sigma_r = 50$ 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$_2$O$_4$ [6, 7]. At temperatures higher than 600°C, isotropic NiFe$_2$O$_4$ films were obtained with the $\sigma_r$ value decreasing slightly as the temperature increased. The film thickness decreased above 700°C due to the powder formation of NiFe$_2$O$_4$ by a homogeneous nucleation in the vapour phase.

3.2. Growth conditions of polycrystalline Ni-Zn ferrite films

Polycrystalline (Ni, Zn)Fe$_2$O$_4$ 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$_2$O$_4$ 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 1 Schematic drawing of the CVD reactor for growing Ni-Zn ferrite films: 1, Ni(acac)$_2$ \cdot 2H$_2$O, 2, Zn(acac)$_2$ \cdot 2H$_2$O, 3, Fe(acac)$_3$; 4, electric resistance furnace; 5, thermocouple; 6, nichrome heater; 7, cooling pipe; 8, substrate; 9, Ni; 10, O$_2$; 11, to rotary pump.](image1)

![Figure 2 Saturation magnetization ($\sigma_r$) of NiFe$_2$O$_4$ films on silica glass plotted against deposition temperature ($T_d$): treatment time = 20 min.](image2)

![Figure 3 X-ray diffraction patterns of (Ni, Zn)Fe$_2$O$_4$ films obtained at various temperatures on silica glass substrate: deposition temperature: (a) 459°C, (b) 550°C, (c) 600°C, (d) 700°C.](image3)

![Figure 4 Thermomagnetic curves of NiFe$_2$O$_4$ and (Ni, Zn)Fe$_2$O$_4$ films: deposition temperature = 600°C.](image4)