JOURNAL OF MATERIALS SCIENCE 21 (1986) 3677–3680

Preparation of nickel and Ni–Zn ferrite films by thermal decomposition of metal acetylacetonates

HIDEAKI ITOH, TADASHI TAKEDA, SHIGEHARU NAKA
Synthetic Crystal Research Laboratory, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464, Japan

Nickel and Ni–Zn ferrite ($Ni_{1-x}Zn_xFe_2O_4$) films were prepared on various substrates (quartz glass, MgO single crystal, etc.) by thermal decomposition of metal acetylacetonates ($Ni(acac)_2 \cdot 2H_2O$, $Zn(acac)_2 \cdot 2H_2O$ and $Fe(acac)_3$). Typical decomposition and heat treatment conditions for obtaining a single phase of $NiFe_2O_4$ film were as follows: evaporation temperature of Ni–Fe complexes: 230° C, the mole concentration of $Fe(acac)_3$, R(%) = $Fe(acac)_3/(Fe(acac)_3 + Ni(acac)_2 \cdot 2H_2O) = 33$, substrate temperature: 330 to 550° C, and heat treatment of the as-grown film: 800 to 1000° C, 1 h. $Ni_{1-x}Zn_xFe_2O_4$ films were obtained by controlling the composition R in Ni–Fe complexes and the evaporation temperature of $Zn(acac)_2 \cdot 2H_2O$. The Ni–Zn ferrite film at the composition $x = 0.37$ ($Ni_{0.63}Zn_{0.37}Fe_2O_4$) gave the maximum saturation magnetization $\sigma_s = 60\,\mathrm{emu\,g^{-1}}$ and the coercive force $Hc \approx 25\,\mathrm{Oe}$. These films showed a magnetic anisotropy which makes the magnetization easy parallel to film surface.

1. Introduction

Ni–Zn ferrite ($Ni_{1-x}Zn_xFe_2O_4$) has been frequently used as magnetic core or head materials, which have a high chemical stability and a low energy loss even in a higher frequency range. Thin film preparation of nickel and Ni–Zn ferrites is increasing its importance especially for the application to microwave devices or magnetic recording systems [1, 2]. Nickel and Ni–Zn ferrite films have been prepared by oxidation of metallic films [3], arc plasma method [4, 5], chemical transport [6, 7] or chemical vapour deposition (CVD) using halide vapour [8–11] or organometallic compounds [12]. Synthesis of spinel ferrite by liquid phase hydrolysis of metal acetylacetonates [13] suggested the possibility of the film preparation from vapour phase. In the present study, nickel ferrite and Ni–Zn ferrite films were obtained by an organometallic CVD (OMCVD) technique which employs the thermal decomposition of metal acetylacetonates. The optimum deposition conditions which control the composition of spinel phase were determined, and the effects of heat treatment of as-grown films on the crystallinity and magnetic properties were investigated.

2. Experimental details

Fig. 1 shows a schematic drawing (a plane figure) of the OMCVD apparatus for preparation of Ni–Zn ferrite films. Three kinds of acetylacetonate complexes, $Ni(acac)_2 \cdot 2H_2O$, $Zn(acac)_2 \cdot 2H_2O$ and $Fe(acac)_3$ were used as starting materials, where acac is an abbreviation of the chelate ligand $CH_3COCHCOCH_3$. By considering the thermodynamic stability of these complexes, nickel (II) and iron (III) acetylacetonates were evaporated from the same quartz boat in the furnace A, and zinc (II) acetylacetonate was evaporated from the other quartz boat in the furnace B. The mixture of nickel and iron acetylacetonates was refluxed in an anhydrous ethyl alcohol for 2 h, and then freed of the solvent under reduced pressure. The mixed powder of these acetylacetonates in the furnace A and the zinc acetylacetonate powder in the furnace B were evaporated, respectively, at given different temperatures. These vapours were carried with nitrogen gas to the deposition furnace (C) in Fig. 1. Oxygen gas as a reactant was introduced directly into the deposition zone by a thin pipe. Soda-lime glass, quartz glass or single crystalline MgO (1 mm × 1 mm × 0.5 mm) was used as the substrate. Prior to the growth experiments of Ni–Zn ferrite films by using the apparatus in Fig. 1, a simple OMCVD furnace which is uniaxial and has only two heating zones for evaporation and deposition, was used for the preparation of nickel ferrite films.

As-grown ferrite films were heat-treated in air in the temperature range from room temperature to 1000° C. X-ray diffraction analysis was performed to identify the deposited species and to determine the composition of spinel phases. The hysteresis loop of the film was measured by vibrating sample magnetometer (VSM).

3. Results and discussion

3.1. Deposition conditions of Ni–Zn ferrite films

Preliminary experiments were carried out to determine the deposition conditions of nickel ferrite ($NiFe_2O_4$)

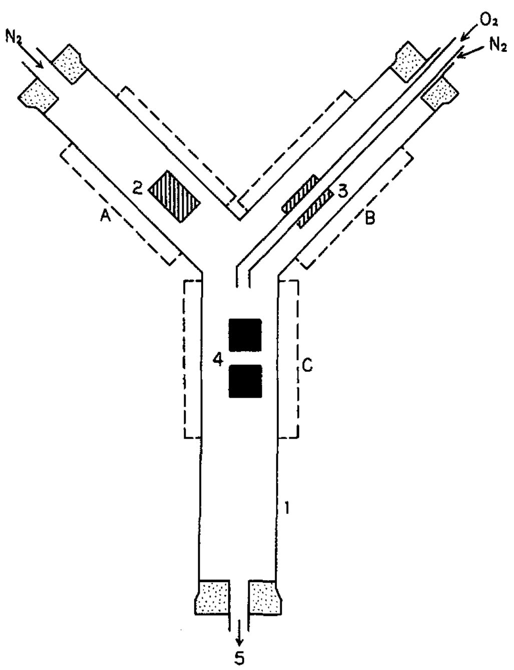

Figure 1 Schematic drawing of organometallic CVD apparatus. 1: quartz reactor, 2: $Ni(acac)_2 \cdot 2H_2O$ + $Fe(acac)_3$, 3: $Zn(acac)_2 \cdot 2H_2O$, 4: substrate, 5: exhaust.

by using the simple OMCVD furnace, as described above. The optimum conditions for deposition of single phase $NiFe_2O_4$ are summarized in Table I. The evaporation temperature of 230° C was chosen to feed an appropriate amount of the Ni–Fe mixed complexes. Amorphous or slightly crystallized films of nickel ferrite were grown at a relatively wide range of substrate temperature (350 to 550° C). The influences of flow rates of nitrogen or oxygen were minor at the flow rates above 200 ml min^{-1} and 20 ml min^{-1}, respectively. The incorporation of free carbon into the film occurred, however, without using oxygen as a reactant gas.

Fig. 2 shows the X-ray diffraction patterns of the films which were deposited and then heat-treated in air at 800° C for 1 h. These films were obtained on the MgO (1 0 0) substrate at various compositions of acetylacetonates. It is convenient to define the mole concentration of $Fe(acac)_3$ in the mixed complexes as $R(\%) = \text{mol}\,Fe(acac)_3/\text{mol}\,\{Fe(acac)_3 + Ni(acac)_2 \cdot 2H_2O\}$. The figure indicates that α-Fe_2O_3 is co-deposited with $NiFe_2O_4$ at higher concentrations of iron acetylacetonate ($R \gtrsim 50$), and a small amount of NiO is detected at lower concentations ($R \gtrsim 30$). The single phase of $NiFe_2O_4$ is obtained apparently at the concentration range, $30 < R < 40$. At the stoichiometric composition of spinel phase, i.e. $R = 66.7$, an excess amount of α-Fe_2O_3 was deposited on account of higher volatility and instability of iron acetylacetonate than those of nickel acetylacetonate. It is suggested by the thermogravimetric analysis of the mixed complexes that no polynuclear complex between iron and nickel acetylacetonates formed during the refluxing procedure.

TABLE I Optimum deposition conditions of $NiFe_2O_4$ film

Evaporation temperature	230° C
Mole concentration of $Fe(acac)_3$	33 mol %
Substrate temperature	350 to 400° C
N_2 flow rate	450 ml min^{-1}
O_2 flow rate	40 ml min^{-1}

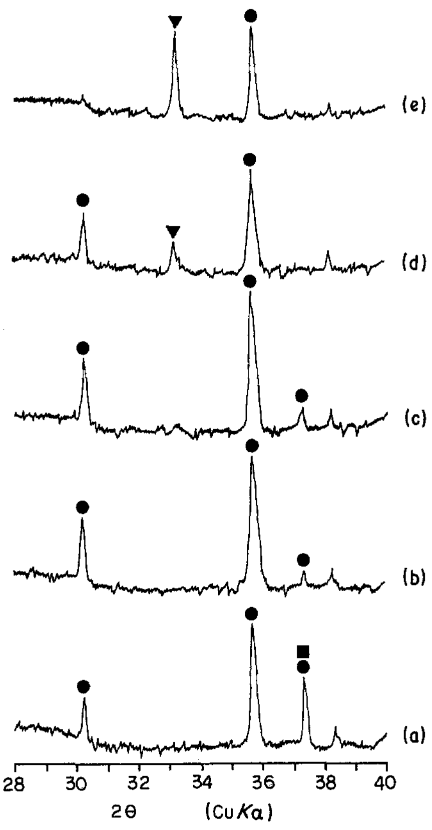

Figure 2 X-ray diffraction patterns of films after heat treatment (at 800° C, 1 h). (●) $NiFe_2O_4$, (▼) α-Fe_2O_3, (■) NiO. Substrate: MgO (1 0 0), mole concentration of $Fe(acac)_3$, $R(\%)$ (a) 25.9, (b) 33.4, (c) 39.9, (d) 50.2, (e) 66.7.

Various compositions of $Ni_{1-x}Zn_xFe_2O_4$ films were prepared by the OMCVD apparatus in Fig. 1. The atomic ratio of Ni/Fe in the spinel phase deposited, was controlled by the value of R, while the atomic ratio of Zn/Fe was controlled by the evaporation temperature of zinc acetylacetonate. The evaporation temperature of nickel and iron acetylacetonate was kept constant at 220° C, which is chosen as a little lower temperature than that (230° C) for deposition of $NiFe_2O_4$, with the aim of depressing the evaporation of Ni–Fe mixed complexes. Table II shows the controlling parameters and the composition (X) of spinel phase. The compositions of $Ni_{1-x}Zn_xFe_2O_4$ were determined from the measured lattice constants of the heat-treated films. It is confirmed from Table II that Ni–Zn ferrite can be obtained by increasing the evaporation temperature of zinc acetylacetonate and simultaneously by decreasing the concentration of nickel acetylacetonate in the Ni–Fe mixed complexes

TABLE II Deposition conditions and compositions of $Ni_{1-x}Zn_xFe_2O_4$ films

R(mol %)	Evaporation temperature of $Zn(acac)_2 \cdot 2H_2O$ (° C)	Composition x
75.0	130	0.64
66.7	140	0.59
60.2	120	0.38
50.2	115	0.36

Evaporation temperature of $Fe(acac)_3$ + $Ni(acac)_2 \cdot 2H_2O$: 220° C.

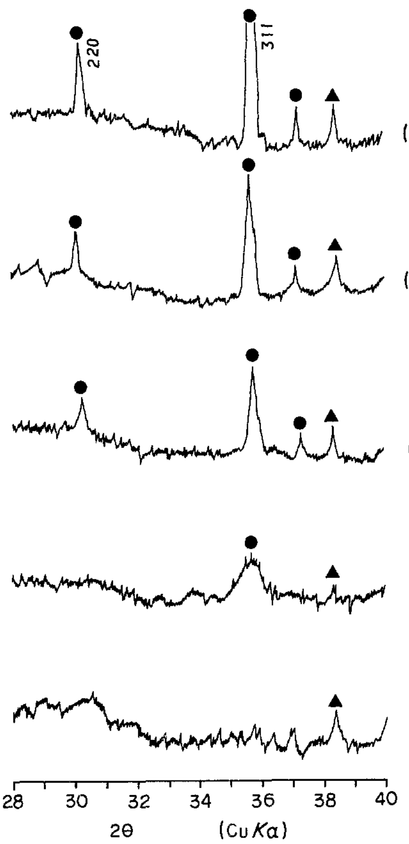

Figure 3 Variation of X-ray diffraction patterns of $NiFe_2O_4$ films with heat treatment. (●) $NiFe_2O_4$, (▲) MgO (a) as-grown film, heat treatment temperature; (b) 500° C; (c) 650° C; (d) 800° C; (e) 1000° C.

powder. Thus, single phase films of the spinel type $Ni_{1-x}Zn_xFe_2O_4$ ($0 \leqq x \leqq 0.6$) were obtained at the substrate temperatures of 350 to 400° C.

3.2. Effects of heat treatment

When $NiFe_2O_4$ was deposited at comparatively high temperatures (~400° C) on both soda-lime glass and quartz glass substrates, as-grown films were slightly crystallized. However, most of the as-grown films on MgO single crystal substrates were less crystalline. This would be due to the adsorption of water vapour onto the MgO surface, which was released from $Ni(acac)_2 \cdot 2H_2O$ at the initial stage of reaction. It was necessary in every case to heat-treat the as-grown films in air at various temperatures in order to increase the crystallinity and the value of the saturation magnetization. Fig. 3 shows the variation of X-ray diffraction patterns of $NiFe_2O_4$ films after the heat treatment for 1 h at 500 to 1000° C. The crystallinity increases as the heat treatment temperature is increased. An isotropic polycrystalline ferrite film with high crystallinity is obtained above 800° C.

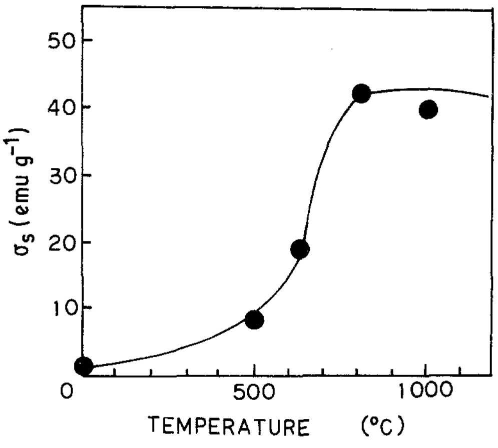

Figure 4 Saturation magnetization against heat treatment temperature. Substrate: MgO (1 0 0), $R(\%) = 33.4$.

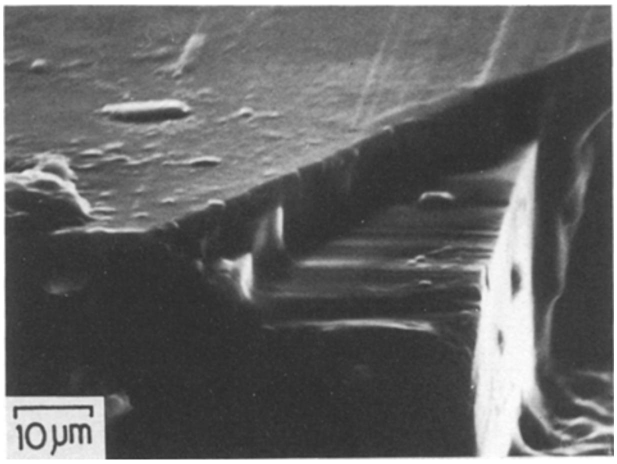

Figure 5 SEM photo of $NiFe_2O_4$ film grown on MgO (1 0 0). Substrate temperature: 350° C, deposition time: 2 h, heat treatment: 800° C, 1 h.

Fig. 4 shows the effect of heat treatment on the magnetization behaviour of $NiFe_2O_4$ film, where the saturation magnetization (σ_s) at room temperature is plotted as a function of heat treatment temperature. Figs 3 and 4 suggest that the saturation magnetization is obviously correlated with the crystallinity of the ferrite film. The considerably low value of σ_s under the heat treatment below 500° C would be due to the superparamagnetism of ultrafine particle sizes of $NiFe_2O_4$ crystallites. The heat treatment at 800 to 1000° C is optimum to obtain the maximum value of σ_s.

As-grown films of $NiFe_2O_4$ on soda-lime glass and quartz glass substrates were occasionally peeled off from the substrate, as the thickness of the films were increased. On the other hand, the ferrite films deposited on the MgO single crystal were adherent to the substrate even after the heat treatment above 800° C. Fig. 5 shows the SEM photo of the $NiFe_2O_4$ film which was grown at the substrate temperature of 350° C on MgO (1 0 0) single crystal and then heat-treated at 800° C for 1 h. A uniform and adherent film with thickness of about 0.8 µm is observed on the (1 0 0) cleavage plane of MgO.

3.3. Magnetic properties of heat-treated films

The composition and crystallinity of the prepared ferrite films have remarkable influences on the magnetic properties of the films. Fig. 6 shows the saturation magnetization of the heat-treated $NiFe_2O_4$ films which is plotted as a function of the mole concentration of $Fe(acac)_3$, R. Comparison with Fig. 2 indicates that the value of σ_s decreases due to a slight incorporation of α-Fe_2O_3 or NiO into the $NiFe_2O_4$ phase. The maximum value of 44 emu g^{-1} was obtained at $R = 33$, where the exact single phase of $NiFe_2O_4$ is

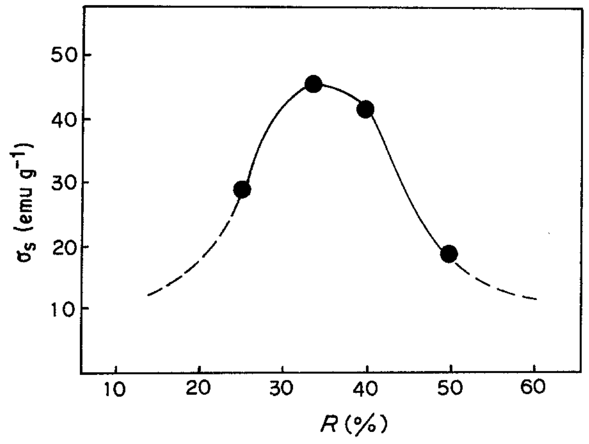

Figure 6 Saturation magnetization against mole concentration ratio (R) of Fe(acac)$_3$. Substrate: MgO (100), heat treatment: 800° C, 1 h.

supposed to be formed. The coercive force Hc was 90 to 170 Oe.

With respect to the Ni–Zn ferrite ($Ni_{1-x}Zn_xFe_2O_4$) films, the highest saturation magnetization of 60 emu g^{-1} was obtained at the composition x = 0.37 ($Ni_{0.63}Zn_{0.37}Fe_2O_4$). The hysteresis loops of $Ni_{0.62}Zn_{0.38}Fe_2O_4$ film are shown in Fig. 7, where the film was grown at 350° C on quartz glass substrate and subsequently heat-treated at 800° C for 1 h. A magnetic anisotropy was confirmed by varying the relative angle between the magnetization direction and the film surface. Magnetization easy direction is found to lie in the film surface as shown in Fig. 7, where $\sigma_s \approx 50$ emu g^{-1} and $Hc \approx 25$ Oe.

4. Conclusions

Various compositions of nickel and Ni–Zn ferrite films were prepared by OMCVD using acetylacetonate complexes of nickel, zinc and iron as starting materials. Thermal decomposition of these compounds was found to proceed on various kinds of substrates at the deposition temperature of 350 to 550° C. This reaction would be accompanied, however, by the oxidation of the thermally decomposed residual reagents. An amorphous or slightly crystalline phase of nickel ferrite was deposited by keeping the evaporation temperature of source powder at 230° C and its composition at R = 33. This phase was confirmed to form a single phase of polycrystalline $NiFe_2O_4$ by subsequent heat treatment of the as-grown film in air above 800° C.

$Ni_{1-x}Zn_xFe_2O_4$ films were prepared by controlling the concentration of Fe(acac)$_3$ in Ni–Fe mixed complexes and simultaneously the evaporation temperature of Zn(acac)$_2 \cdot 2H_2O$. The saturation magnetization (σ_s) of these films was found to increase with the increase in the heat treatment temperature. It is confirmed from the hysteresis loop of Ni–Zn ferrite films that the maximum value of σ_s = 60 emu g^{-1} was obtained at the ferrite composition x = 0.37 ($Ni_{0.63}Zn_{0.37}Fe_2O_4$) with the coercive force Hc = 25 Oe.

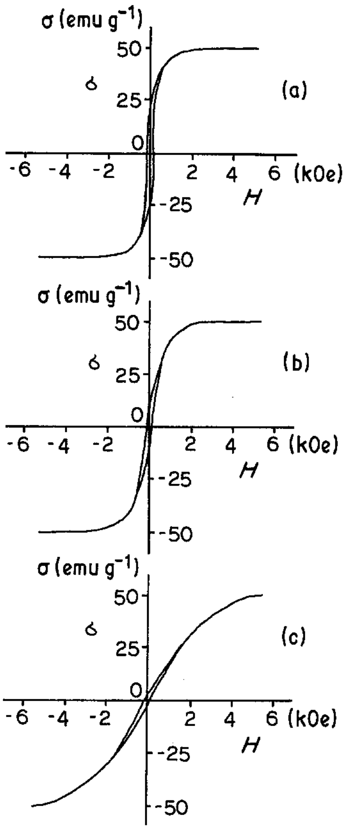

Figure 7 Hysteresis loop of $Ni_{0.62}Zn_{0.38}Fe_2O_4$ film. Angle between the magnetic field direction and the film surface direction: (a) 0°; (b) 45°; (c) 90°.

References

1. E. HIROTA, K. HIROTA and K. KUGIMIYA, in Proceedings of the 3rd International Conference on Ferrites, Tokyo, September 1980 (Center for Academic Publications, Tokyo, 1981) p. 667.
2. J. P. LAZZARI, in Proceedings of the 3rd International Conference on Ferrites, Tokyo, September 1980 (Center for Academic Publications, Tokyo, 1981) p. 695.
3. G. SURAN and A. HEURTEL, *J. Appl. Phys.* **43** (1972) 536.
4. J. F. DILLON Jr, *ibid.* **41** (1970) 1348.
5. M. NAOE and S. YAMANAKA, *Jpn. J. Appl. Phys.* **9** (1970) 293.
6. D. J. MARSHALL, *J. Cryst. Growth* **9** (1971) 305.
7. P. GIBART, M. ROBBINS and A. B. KANE, *ibid.* **24/25** (1974) 166.
8. G. R. PULLIAM, *J. Appl. Phys.* **38** (1967) 1120.
9. J. E. MEE, G. R. PULLIAM, J. L. ARCHER and P. J. BESSER, *IEEE Trans. Mag.* **MAG-5** (1969) 717.
10. A. G. FITZGERALD and R. ENGIN, *Thin Solid Films* **20** (1974) 317.
11. S. ITO, H. MIYASHITA and N. YONEDA, in Proceedings of the 3rd International Conference on Ferrites, Tokyo, September 1980 (Center for Academic Publications, Tokyo, 1981) p. 733.
12. L. BEN-DOR, R. DRUILHE and P. GIBART, *J. Cryst. Growth* **24/25** (1974) 172.
13. Y. SUWA, S. HIRANO, K. ITOZAWA and S. NAKA, in Proceedings of the 3rd International Conference on Ferrites, Tokyo, September 1980 (Center for Academic Publications, Tokyo, 1981) p. 23.

Received 5 November 1985
and accepted 10 January 1986