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Preparation of (Zn, Fe)Fe₂O₄ Thin Film by MOCVD

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Abstract. (Zn,Fe)Fe₂O₄ thin films have been prepared by MOCVD, applying a novel evaporation method for MO reagents; Zn(acac)₂ and Fe(acac)₃. These reagents were mixed with a composition of Fe/Zn=0.5-2.0 and were then completely vaporized at 215°C. By the use of single evaporation vessel, the arrangement of MOCVD apparatus has been simple. The vapors with a constant ratio were evolved from the vessel to deposition zone to react with oxygen at 500°C for 30 min. The reproducibility was established on the relationship between mixing ratio and film composition. In addition, high crystallinity was obtained even at 500°C without annealing at higher temperature. The magnetic properties of the Zn_{0.73}Fe_{0.27}Fe₂O₄ thin film were measured as 38 emu/g and 110 Oe at 25°C.

1. INTRODUCTION

In MOCVD using powder reagents, the composition control of the deposited film of complex oxide such as ferrite is generally difficult. This is because the evaporation rate of each MO reagent is not constant during the film deposition. On the other hand, the vapor composition would be constant, if mixed MO reagents were completely vaporized in a vessel. In addition, the amount of the reagents required to make a thin film is not so much. In this study, the vapors were supplied from a vessel containing a constant composition of the MO vapors. This novel method has been applied to the film growth of (Zn,Fe)Fe₂O₄, in which reproducibility of the composition and magnetic properties of the film were investigated.

2. EXPERIMENTAL

Figure 1 shows schematic diagram of the apparatus. The apparatus became simple compared with the conventional one, because of single evaporation vessel without carrier gas. Two kinds of acetylacetonate complexes, Zn(acac)₂ and Fe(acac)₃ were selected as MO reagents. These reagents (total amount : ca. 0.2g) were mixed with a composition of Fe/Zn=0.5-2.0 and charged into the evaporation vessel. After evacuating the system under 5 Torr, leak valve was closed and the vessel was heated at 215°C to vaporize the mixed reagents completely. The leak valve was then opened to evolve the vapor with a constant composition. The vapors were transported to the deposition zone to react with oxygen (0-200 ml/min) and deposited on a borosilicate glass (9x9x0.2mm) at 500°C for 30min. The deposited films were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The film composition was determined by inductively coupled plasma emission spectrometry. The magnetic properties of the film were measured by vibrating sample magnetometer.

Figure 1 : MOCVD apparatus for (Zn, Fe) Fe₂O₄ thin films.

3. RESULTS AND DISCUSSION

3.1 Determination of evaporation temperature

Fe(acac)₃ (0.2g) powder was completely vaporized by heating an evaporation vessel at 210°C. α - Fe₂O₃ film was obtained by the reaction of the vapor and oxygen (100 ml/min). When Zn(acac)₂ powder (0.2g) was heated in the the vessel at 140°C, the powder was disappeared. ZnO thin film oriented (100) was obtained by the reaction of the vapor and oxygen (100 ml/min). Therefore, the evaporation temperature of the mixed reagents was determined as 215°C.

3.2 Determination of oxygen flow rate

Figure 2 shows X-ray diffraction pattern of the film obtained at 500°C under the oxygen flow rate of 150 ml/min. The pattern was clearly identified as that of spinel phase. The film thickness was estimated to be ca. 1 μm, which was calculated from the amount of deposit determined by chemical analysis. It was the maximum under this oxygen flow rate. Using a conventional apparatus, Mn-Zn ferrite and Ni-Zn ferrite thin films obtained at 500°C required to be annealed at higher temperature to obtain the crystallinity and high magnetization [1, 2]. In our apparatus, the vapors would be supplied with a constant ratio during the film growth. Therefore, the film with high crystallinity may be obtained even at 500°C.

3.3 Reproducibility of the film composition and the magnetic properties

Under the suitable conditions described above, the films were deposited at different mixing ratios of MO reagents. The compositions obtained were 1.05, 2.47 and 3.35, against 0.5, 1.0 and 2.0 of the mixing ratios, respectively. The films contained excess amount of Fe. The vapor species of Zn(acac)₂ may be decomposed at lower temperature region of the furnace. Figure 3 shows the relationship between film composition and mixing ratio of MO reagents; Fe/Zn=0.8-1.1. The film composition was controlled by selecting the mixing ratio of the reagents. At Fe/Zn=0.9, the stoichiometric ZnFe₂O₄ film was obtained. According to SEM observation, the film consisted of fine grains with ca. 0.1 μm. Table 1 shows saturation magnetization and coercive force of the films. Although stoichiometric ZnFe₂O₄ is not ferromagnetic material, (Zn,Fe)Fe₂O₄ would reveal the magnetization due to Fe²⁺. Table 1 also gives σ₀ values calculated from the data in Ref. 3. The large difference from σ_s and σ₀ indicates that ion distribution in the deposit may be different from that in equilibrium state. It is concluded that the novel evaporation method contributes the reproducibility and the crystallinity of the film obtained by MOCVD.

Figure 2 : XRD pattern of thin film deposited on a borosilicate glass substrate.

Mixing ratio of MO reagents:Fe/Zn=2.0, Flow rate of O₂:150 ml/min, Deposition temperature:500°C, Deposition time:30 min.

Figure 3 : Relationship between film composition and mixing ratio of MO reagents.

Flow rate of O₂:150 ml/min, Deposition temperature:500°C, Deposition time:30min.

Table 1 : Saturation magnetization (σ_s) and coercive force (Hc) of the films (at 25°C).

Film	σ _s (emu/g)	σ ₀ (emu/g) ³⁾	Hc (Oe)
Zn _{0.86} Fe _{0.14} Fe ₂ O ₄	19	—	116
Zn _{0.83} Fe _{0.17} Fe ₂ O ₄	18	—	84
Zn _{0.73} Fe _{0.27} Fe ₂ O ₄	38	126	110
Zn _{0.54} Fe _{0.46} Fe ₂ O ₄	16	131	50
Zn _{0.14} Fe _{0.86} Fe ₂ O ₄	30	117	98

Flow rate of O₂:150 ml/min, Deposition temperature:500°C, Deposition time:30 min

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