Low-Pressure MOCVD of Fe$_3$O$_4$ Epitaxial Thin Films, and Their Surface Reaction Process

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The crystalline quality and deposition mechanism of iron oxide films prepared by metalorganic chemical vapor deposition (MOCVD) at low pressure were investigated. The films were deposited at substrate temperatures of above 673 K. RHEED measurements showed that Fe$_3$O$_4$ thin films epitaxially grown on c-plane sapphires have excellent crystal quality and extremely flat surfaces. The deposition process for the films was well explained by the Langmuir–Hinshelwood mechanism, in which an oxidation reaction occurs between molecules of an iron source and oxygen adsorbed onto the surface. These results suggested that atomic layer epitaxy of ferrite thin films may be achieved by alternately adsorbing the iron source and the oxygen.

Key words: Fe$_3$O$_4$ film, MOCVD, epitaxial growth, surface reaction process, adsorption, Langmuir–Hinshelwood mechanism, atomic layer epitaxy

1. Introduction

Thin films of magnetic spinel ferrites having wide electrical conductivity of insulator to metal are of great interest as potential materials for advanced applications such as microwave devices and spin-tunneling devices. These applications require a precisely controlled growth of the ferrite films with high crystalline quality. Metalorganic chemical vapor deposition (MOCVD) which is widely used for growth of semiconducting films is a candidate satisfying the requirement. This is because it is free from crystal-damage with bombardment of high energy particles which induces serious problems in physical vapor deposition represented by sputtering. Several studies on MOCVD of the spinel ferrite films and hexaferrite films have been reported in the past.

However, few studies on the reaction process which is a significant factor dominating the film growth have been done so far, exclusive of recent works on thermal or plasma-assisted dissociation of iron source during transport. One of the reasons is that the films were conventionally deposited at relatively high pressure, i.e., under viscous flow in which a stagnant layer was formed around the substrate surface, and crystalline nucleation in gas phase made the discussion of the film-deposition process complicated.

In the present study, we have deposited iron oxide films by MOCVD at low pressure without the viscous flow. Objectives of this paper are to demonstrate the high potential of this method for obtaining Fe$_3$O$_4$ epitaxial films with high quality and to clarify reaction mechanism in the low pressure MOCVD. In addition, we refer to a possibility of atomic layer epitaxy of the ferrite thin films.

2. Experimental

The films were grown by the low pressure MOCVD using a cold wall reactor. The reactor was evacuated to a base pressure of the order of 10$^{-7}$ Torr prior to the film deposition. Ferric acetylacetonate Fe(C$_5$H$_7$O$_2$)$_3$ precursor was used as the iron source. This precursor was carried to the reactor by a flow of argon after vaporized in a reservoir held at 393 K. The pressure of Fe(C$_5$H$_7$O$_2$)$_3$ precursor vapor without the carrier gas flow was 3×10$^{-4}$ Torr in the reactor chamber. After mixed with oxygen, the carrier gas flow was supplied onto substrate surface through a nozzle about 40 mm away from the substrate. The pipe-line transporting the precursor vapor was heated to 403 K to prevent the source materials from coagulating. The flow rates of oxygen and argon were varied in the range of 0 to 3 ccm by mass flow controllers. The total flow rate and the total gas pressure were normally kept at less than 5 ccm and less than 1×10$^{-3}$ Torr, respectively. This gas pressure satisfies a molecular flow condition because the mean free path of the Fe(C$_5$H$_7$O$_2$)$_3$ molecule is longer than the distance between the outlet of the nozzle and the substrate. Single crystals of (111)-oriented gadolinium gallium garnet (GGG) and basal c-plane sapphires were used as the substrates for determining deposition parameters and for epitaxial growth, respectively. These were heated up to 823 K.

The structural quality and the surface morphology of the deposited films were characterized by X-ray diffractometry, reflection high-energy electron diffraction (RHEED) and scanning electron microscopy.

3. Results and Discussion

3.1 Film growth and crystalline quality

All films deposited on GGG substrates were polycrystalline. Figure 1 shows the deposition rate of the film at a substrate temperature ($T_s$) of 723 K, plotted as a function of oxygen flow rate ($R_O$). The deposition rate
rapidly increased with elevated \( R_o \) and tended towards a limit dependent on the flow rate of the carrier gas (\( R_c \)). The limits were 0.33 nm/min at \( R_c=1 \) ccm and 0.57 nm/min at \( R_c=2 \) ccm. Figure 2 shows relationship between the deposition rate and \( T_s \) for the films deposited at \( R_o=3 \) ccm and \( R_c=2 \) ccm. The film growth occurred above 673 K. The deposition rate remarkably increased with \( T_s \) and reached a maximum at 723 K. These results indicate that the amount of the Fe(C₈H₂O₄)₃ precursor supplied to the substrate surface is the rate-determining factor for \( R_o > 1 \) ccm and \( T_s \geq 713 \) K. The reduction of the growth rate above 723 K seen in Fig. 2 is associated with a surface reaction process as discussed later. Figure 3 shows the crystalline phase diagram for the films deposited at (a) \( T_s = 748 \) K and (b) \( T_s = 698 \) K at various flow rates of oxygen and the carrier gas. When \( R_o \) was lower than a threshold value, no film was deposited on the substrate. The threshold value increased with \( R_c \) increasing and/or \( T_s \) decreasing. With the increase of \( R_o \), the films at \( T_s = 748 \) K crystallized in spinel phase and/or in corundum phase. However, spinel single phase was not observed for the films deposited at \( T_s = 698 \) K. The dependence of formed crystalline phase on \( R_o \) are qualitatively similar to that on the oxygen partial pressure in the equilibrium diagram of Fe-O. However, it should be noted that the \( R_o \) region of no film-deposition exists and the scale of the oxygen partial pressure in Fig. 3 is greatly deviated from that in the equilibrium diagram. For example, the oxygen pressure at which Fe₃O₄ is stable is about \( 2 \times 10^{-4} \) Torr (1 ccm) at 748 K in our experiment, while \( 1 \times 10^{-15} \) Torr in the equilibrium diagram. These two facts were observed in the epitaxial growth of Fe₃O₄ films on sapphire as well, associated with a growth mechanism discussed later.

Figure 4 shows (a) \( \theta/2\theta \) and (b) \( \phi \) scans of X-ray diffraction and (c) RHEED profile for the Fe₃O₄ thin film (60-nm thick) deposited on c-plane sapphire at \( T_s = 748 \) K \( (R_c = 1 \) ccm and \( R_o = 0.6 \) ccm). The film had strong [hhh] orientation normal to the film plane. The \( \phi \) scan of the Fe₃O₄ (220) reflections measured at an angle of 35.3° to the film surface showed six sharp peaks every 60° (Fig. 4(b)), which indicates the presence of double domain structure. These peaks made a \( \phi \) angle of 30° with those taken from the (1014) planes of the substrate. These results indicate that a (111)-oriented single crystalline film of Fe₃O₄ is grown on c-plane sapphire with an in-plane alignment of Fe₃O₄ [110] parallel to sapphire [1100]. The lattice mismatch between the film and the substrate calculated from the lattice constants at room temperature is as large as 7.9%. Nevertheless, RHEED taken along the [112] azimuth of the Fe₃O₄ film exhibited extremely streaky pattern with reflections from the higher order Laue
zones as shown in Fig. 4(c). This suggests that the film has excellent crystalline quality and extremely flat surface.

3.2 Surface reaction mechanism

Figure 5 illustrates reaction processes possible for MOCVD of the oxide film at low pressure. The process (a) is the case that the transported Fe(C₅H₇O₂)₃ precursor or thermally dissociated one directly reacts with the reactant oxygen which is in the gas phase. This process has been conventionally discussed in earlier works. Others include an adsorption process; the Fe(C₅H₇O₂)₃ precursor is the process (b) or oxygen in the process (c) is adsorbed on the surface and subsequently reacts with the other reactant in the gas phase (Eley–Rideal mechanism). In the process (d), oxidation reaction occurs between adsorbates on the surface (Langmuir–Hinshelwood mechanism).

Two significant facts have to be taken into account on assessment of these processes. One is the amount of oxygen required for the film deposition. The impinging rate of oxygen onto the surface calculated from the oxygen partial pressure of $6 \times 10^{-4}$ Torr ($R_0 = 3$ ccm) was about $2 \times 10^{-7}$/cm$^2$·s. On the other hand, that of the Fe(C₅H₇O₂)₃ precursor estimated from the partial pressure of the vapor ($2.7 \times 10^{-6}$ Torr) was about $5 \times 10^{-3}$/cm$^2$·s. This value is in consistent with that estimated from the supplied amount of the iron source of $1.1 \times 10^{-4}$ mol/min in the literature. The amount of oxygen to the Fe(C₅H₇O₂)₃ molecule on the substrate surface is, therefore, about $10^4$, much larger than the value of $17/4$ required for completely oxidizing the iron source by the following chemical reaction:

$$4\text{Fe(C}_5\text{H}_7\text{O}_2)_3 + 17\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 30\text{CO} + 10\text{CO}_2$$

+ $20\text{CH}_4 + 2\text{H}_2\text{O}$. (1)

Such excess oxygen required for the film deposition cannot be explained by the process (a) and (b) in which oxygen is directly supplied from the gas phase. This suggests the presence of adsorption process of oxygen as seen in the process (c) and (d).

Another experimental fact is the presence of the threshold amount of oxygen below which the film is not deposited. Figure 6 shows temperature dependence of the threshold amount of oxygen required for depositing the film at $R_c = 2$ ccm. The threshold amount of the oxygen partial pressure increased exponentially with $T_i$ decreasing. This result is discrepant with that expected from the process (c). This is because the adsorption of oxygen rather increases at low temperature, which results in reduction of the oxygen partial pressure required for the oxidation reaction.

On the other hand, the process (d) explains all of the above results well. Using the partial pressure of the Fe(C₅H₇O₂)₃ precursor vapor, $P(Fe)$, and that of oxygen, $P(O_2)$, the rate of reaction, $V$, in this process is described.

![Fig. 5](image_url)

Surface reaction processes possible for MOCVD of iron oxide film at low pressure.
Fig. 6 Temperature dependence of the minimum oxygen partial pressure required for depositing films at $R_c = 2$ ccm.

\[ V = k \theta(\text{Fe}) \theta(\text{O}_2) \]

\[ \theta(\text{Fe}) = K(\text{Fe}) P(\text{Fe}) / [1 + K(\text{Fe})P(\text{Fe}) + K(\text{O}_2)P(\text{O}_2)] \]

\[ \theta(\text{O}_2) = K(\text{O}_2) P(\text{O}_2) / [1 + K(\text{Fe})P(\text{Fe}) + K(\text{O}_2)P(\text{O}_2)] \]

where, $k$ is a rate constant, $\theta(\text{Fe})$ and $\theta(\text{O}_2)$ fractional coverages of $\text{Fe(C}_x\text{H}_y\text{O}_z\text{)}$ molecules and $\text{O}_2$ molecules on the surface, respectively. It was assumed here that the adsorption is described by the Langmuir isotherm without dissociation of the molecules. $K(\text{Fe})$ and $K(\text{O}_2)$ denote the ratio of the rate constant of adsorption to that of desorption for $\text{Fe(C}_x\text{H}_y\text{O}_z\text{)}$ and oxygen, respectively. Since $K(i) (i = \text{Fe}, \text{O}_2)$ is a thermodynamical equilibrium constant, it is in general expressed by the following Eqs. (5) and (6), using the standard reaction Gibbs function $\Delta G(i)$ which is negative for the spontaneous adsorption process with exotherm:

\[ K(i) = \exp \left[ -\Delta G(i) / k_B T_s \right] \quad (i = \text{Fe}, \text{O}_2) \]

\[ \Delta G(i) = \Delta H(i) - T_s \Delta S(i) \]

where $\Delta H(i)$ and $\Delta S(i)$ denote standard reaction enthalpy and standard reaction entropy, respectively, $k_B$ Boltzmann constant. The combustion of the precursor according to Eq. (1) is obtained when the relationship $\theta(\text{O}_2) = 17 \theta(\text{Fe})/4$ is satisfied. This relationship is rewritten using Eqs. (3), (4), (5), and (6):

\[ P(\text{O}_2) = [17A(\text{Fe})/4A(\text{O}_2)] P(\text{Fe}) \exp \left[ (1/k_B) \Delta S(\text{Fe}) - (1/k_B) \Delta S(\text{O}_2) \right] \exp \left[ (1/k_B) \Delta H(\text{O}_2) - \Delta H(\text{Fe}) \right] \]

Since $\Delta H(\text{Fe}) < \Delta H(\text{O}_2) < 0$ for the adsorption onto the oxide substrate, the minimum $P(\text{O}_2)$ required for the reaction exponentially increases with $T_s$ decreasing. Equation (7) explains the $T_s$ dependence of the minimum $P(\text{O}_2)$ shown in Fig. 6 well. From the inclination of the line in Fig. 6, $\Delta H(\text{O}_2) - \Delta H(\text{Fe})$ was obtained as 92 kJ/mol. Thus, the large amount of oxygen required for depositing the film is due to the adsorption amount of oxygen much less than that of $\text{Fe(C}_x\text{H}_y\text{O}_z\text{)}$ precursor onto the substrate surface. The reduction of the deposition rate at high temperature shown in Fig. 2 is also explained in terms of the decrease of the adsorption amount of $\text{Fe(C}_x\text{H}_y\text{O}_z\text{)}$ precursor on the surface.

The above mechanism derives a much interested result; the epitaxial growth of ferrite thin film controlled layer by layer, so-called atomic layer epitaxy, may be achieved by alternately adsorbing the $\text{Fe(C}_x\text{H}_y\text{O}_z\text{)}$ precursor and oxygen. This technique makes it possible to grow the ferrite film with extremely high quality.

4. Conclusion

We have prepared iron oxide films by MOCVD at low pressure without viscous flow. The films were deposited at $T_s \sim 673 \text{ K}$. The crystalline phase of the films changed from spinel to corundum with the oxygen partial pressure increasing for a constant supply of the iron source. RHEED measurements showed that $\text{Fe}_9\text{O}_4$ thin films epitaxially grown on c-plane sapphires have excellent crystal quality and extremely flat surface. However, when the oxygen partial pressure is less than a threshold, no film was deposited. The threshold value of the $P(\text{O}_2)$ increased exponentially as the substrate temperature was reduced. In addition, it was found that the amount of oxygen $10^7$ times larger than that of the iron precursor is required for the film deposition. These results were well explained in terms of the Langmuir–Hinshelwood mechanism in which an oxidation reaction occurs between molecules of $\text{Fe(C}_x\text{H}_y\text{O}_z\text{)}$ and oxygen adsorbed onto the surface. This suggests that atomic layer epitaxy of ferrite thin films may be achieved by the alternate adsorption of the iron source and the oxygen.

References


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