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Fabrication of Iron Films by Thermal CVD with Imposition of Magnetic Field

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Abstract

Iron films were fabricated by means of thermally activated Chemical Vapor Deposition (thermal CVD) with imposition of magnetic field up to 3.5 tesla (T). Effects of imposing magnetic field on the CVD process, the microstructure and the crystal orientation of the deposits were investigated. Iron chloride ($FeCl_3$) was utilized as the precursor. The vapor was reduced with hydrogen and iron films were deposited on SiO_2 substrate in a temperature range between 873 and 973K. Weight loss of the source chloride increased as an increase of the magnetic field intensity. This phenomenon might be related to the increase of the supply rate of gas source due to attraction of the chloride vapor by magnetic field.

Island- and film-state deposits were obtained depending on the deposition conditions. It was demonstrated that the films were formed by coalescence of the island crystals. Population of the cube-shaped island crystals increased with an increase of the magnetic field, and the degree of (100) orientation increased. On the other hand, the film-state deposits did not have preferred orientations. We discussed the difference in the features of crystal orientation considering the grain structures of the deposits.

Key words: chemical vapor deposition, iron, magnetic field, orientation, morphology

1. Introduction

Recently, availability of strong magnetic field increased along with the development of cryogen-free magnets [1]. Therefore, it became possible not only to investigate material properties but also to fabricate materials by imposition of a strong magnetic field.

In these trends, fabrication of vapor deposited films has been attempted by imposition of strong magnetic field. There are couples of studies performed for physical vapor deposited (PVD) films. Fe and Fe-Si-O films are fabricated by means of sputtering [2, 3]. Pt-Fe films by laser ablation [4], and Bi films by evaporation [5] are the examples. In these studies, relationships between the imposition conditions and the crystal orientation of films have been discussed frequently. On the other hand, a few attempts have been made for chemical vapor deposited (CVD) films. Fabrication of YBCO superconducting oxide [6] by application of magnetic field is the example.

In some of the PVD techniques (sputter, and laser ablation), plasma plays an important role in film deposition, which has a strong interaction with the magnetic field and usually accompanied the processes with difficulties to control their states. On the other hand, in the thermal CVD process, gas flow is not influenced by Lorenz force, and expected to be easier to control. Moreover, in this process substrate temperature is usually high, as the reaction is thermally activated. Therefore, the microstructural evolution can occur the deposited solid film, such as the grain boundary migration and the grain growth, which are related to the orientation of the film crystals.

This study attempts fabrication of iron films by thermal CVD with imposition of magnetic field. Because iron is a ferromagnetic material, it is expected that imposition of magnetic field has larger effect than to the other non-magnetic materials, if the deposition temperature is below Curie point. In this study, it is aimed to investigate the effect of magnetic field on the CVD process, the film microstructures and the crystal orientations.

2. Experimental

Iron film was chemical-vapor-deposited by reducing an iron chloride ($FeCl_3$) vapor with hydrogen, according to the following overall reaction:

$$2FeCl_3(g) + 3H_2(g) = 2Fe(s) + 6HCl(g)$$

The vaporization and substrate temperatures are listed in Table 1, together with the other process conditions. Range of the substrate temperature corresponds to about 0.48 to $0.54T_m^{Fe}$ (T_m^{Fe} : melting point of iron) and is below the Curie Point of Fe($0.58T_m^{Fe}$)

Because of difficulty to control the gas path heated at the vaporization temperature (>450K), the reactor and the vaporizer are confined in a same tube made of quartz, as schematically illustrated in Fig. 1. Tube was placed inside of the magnetic bore (22cm in diameter) vertically, and the gas mixture consisting of $FeCl_3$ vapor with Ar carrier, and hydrogen were blown upward from the bottom of the tube. Amorphous SiO_2 plate (10x8x0.5mm) was used for the substrate and was set on a holder made of stainless steel (type SUS316). Electric heater made of SiC was used for heating the substrate, and was surrounded by a water-cooled Cu coil. The tube was evacuated. The operation pressure and the gas flow rates were controlled as listed in Table 1.

In this study, weight changes of the gas source ($FeCl_3$) before and after the CVD processes were measured. Film microstructures were observed by means of an optical microscope (OM), a field emission scanning electron microscope (FE-SEM) and a transmission electron microscope (TEM). Film crystal orientation was characterized by means of X-ray diffraction (XRD). Normal θ-2θ scan and rocking curve (ω scan) techniques were conducted. The ω scanned data was corrected by means of TexturePlus [7].

Table1. Experimental conditions

Substrate temperature/K	873～973
Vaporizer temperature/K	503
Magnetic flux density/T	0～3.5
Total pressure/Torr	100
H_2 gas flow rate/cc min^{-1}	110, 220
Ar gas flow rate/cc min^{-1}	30, 60
Deposition time/min	30, 60

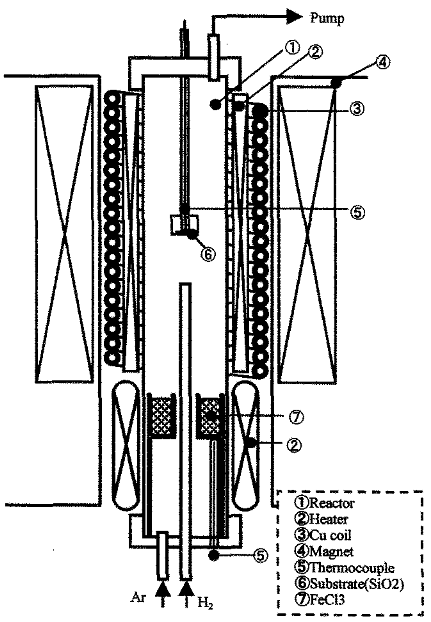


Fig.1 Experimental apparatus.

3. Results

3.1 Influence of magnetic field on the CVD process

It was demonstrated that consumption of the chloride gas source was dependent on the magnitude of magnetic field. The relationship between the magnetic field and the weight change of the vaporizer is plotted in Fig. 2 (vaporization temperature at 503K). In spite of scattering of the data, the plot indicates a tendency that consumption of the chloride became larger as an increase of the magnetic field. When 4.4T was imposed at the same vaporization temperature, the chloride transported too much, and choking of H_2-nozzle occurred. Effect of the magnetic field was significant. However no data at 4.4T was plotted in Fig. 2.

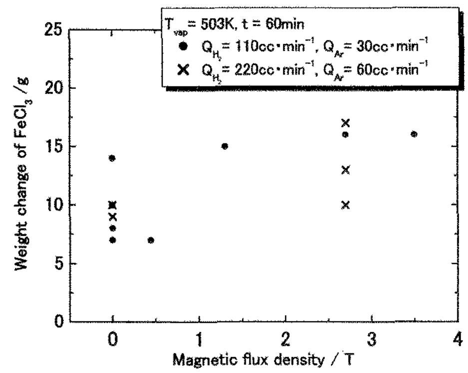
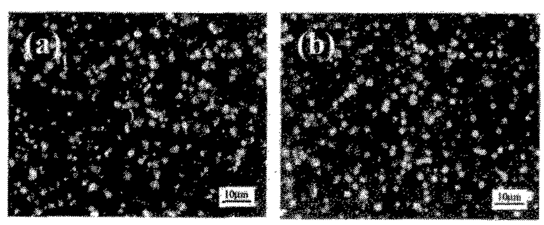


Fig.2 Relationship between magnetic flux density and weight change of $FeCl_3$.

3.2 Observation of the deposited states

The iron deposits were observed by means of OM. Morphologies of the island-state crystals deposited at 873K are shown in Fig. 3(a) and (b). The islands are mostly isolated but some of them are coalesced. They have polyhedral shapes and are facetted. In the case without imposition of magnetic field, different polyhedrons are seen and they are oriented in different ways (Fig. 3(a)). On the other hand, when magnetic field of 2.7T is imposed, cube-shaped islands increased their population (Fig. 3(b)). The magnetic field enhanced formation of the cube-shaped crystals and standing them with their {100} planes parallel to the substrate.

In a FE-SEM photograph shown in Fig. 3(c), there are coalesced islands. It is considered that the iron films are formed by further coalescence of these island-state crystals.



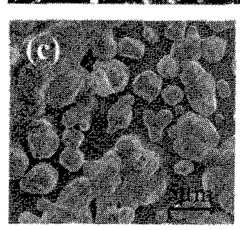


Fig.3 Optical micrograph [(a), (b)] and FE-SEM micrograph [(c)] of Fe deposits (island-state). (a)Without magnetic field (b)With magnetic field (2.7T) (c)With magnetic field (2.7T)

3.3 Crystal orientation of the films

θ-2θ scanned XRD profiles from the island-shaped crystals are shown in Fig. 4(a). (200)-peak intensity increased by imposition of a magnetic field of 2.7T. In bcc-iron crystal, (110) peak is the highest peak in the random orientation state. Increase of (200) peak intensity is related to the {100}-preferred orientation of the deposited crystals. In order to obtain the more quantitative information on the preferred orientation,

ω-scan was performed. Variation of ω- scanned (200) peak intensities (rocking curve) with the magnitude of magnetic field is shown in Fig. 4(b). They are all obtained from the island-shaped deposits at 873K. It is seen that the peak became sharper as an increase of the field strength, indicating the increase of the degree of (100) preferred orientation.

An iron film was also deposited at 873K by imposition of 2.7T. The ω-scanned peaks from the island- and film-state crystals are compared in Fig. 4(c). The (100)-preferred orientation was not observed in the film-stated crystals.

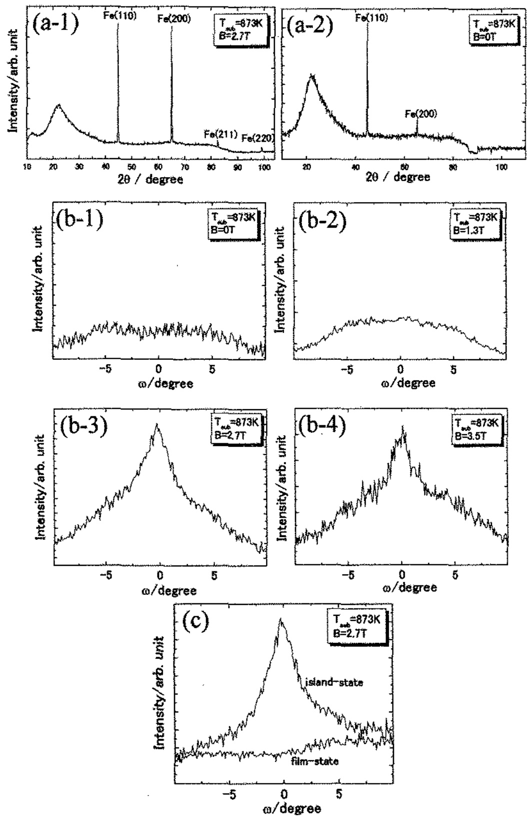


Fig.4 XRD-patterns and Rocking curves.
(a-1,2) θ -2 θ scanned XRD-patterns of Fe (island-state).
(b-1,2,3,4)Rocking curves (ω- scanned patterns) for (200) plane of Fe (island-state)
(c)Rocking curves for (200) plane of Fe (island and film state)

3.4 TEM observation

In order to obtain the local crystallographic and morphological information of the iron deposits, TEM observation was performed. In Fig. 5, a cube-shaped island crystal deposited at 873K, 2.7T is shown. The edges of the cube are rounded in this case, which correspond to the SEM photograph in Fig. 3(c). The electron diffraction (ED) pattern (Fig. 5) from this island-shaped crystal indicates that its growth direction (<100>) is perpendicular to the substrate and parallel to the direction of magnetic field. These island-shaped crystals are related to the (100) preferred orientation.

In Fig. 6, TEM images of a film cross section are shown. The film was deposited at 873K, 2.7T. There are three grains in the view, from which ED patterns were obtained. It was demonstrated that their crystal orientations are different. The grains in both sides had almost similar directions of <100> axises. However, one is rotated from the other. The intermediate grain has completely different direction. The grain size had similar scale to the film thickness. The grains are not classified to the columnar grain, but to the recrystallized grains.

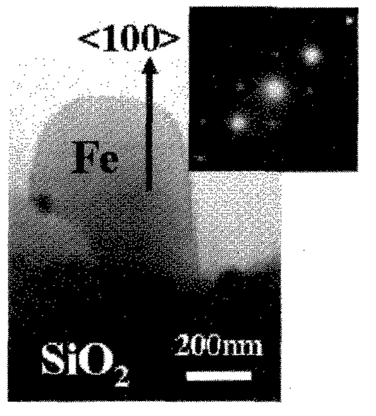


Fig.5 TEM micrograph of Fe (island-state) deposited by imposition of magnetic field (2.7T).

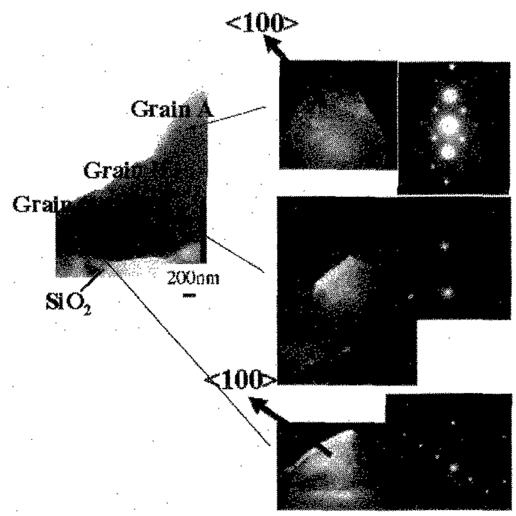


Fig.6 TEM micrograph of Fe (film-state) deposited by imposition of magnetic field (2.7T).

5. Discussion

1, Effect of Magnetic field on the CVD process.

As shown in Fig. 2, weight loss of the $FeCl_3$ source was dependent on the imposed magnetic field. The vaporized $FeCl_3$ flows through an area where strong magnetic field gradient existed. $FeCl_3$ is paramagnetic above Neel temperature (T_N=20K), and the magnetic susceptibility is estimated to be $\chi_{FeCl3}=8.6x10^{-5}$ at room temperature, which is much larger than the other gas (cf. χ_{O2} : $1.52x10^{-7}$).

The source gas might be attracted to the magnet center. In such circumstances, a larger amount of the vapor might be transported from the vaporizer in order to keep the constant vapor pressure.

There might be a dependence of the film growth rates on the imposed magnetic field, because of its effects on the mass transfer rates. However, it was not demonstrated in this study, as the growth rates cannot be compared in the same background. It was necessary to adjust the distance between the H_2 nozzle and the substrate at each condition, for the purpose of avoiding deposition of $FeCl_2$.

2. Difference in the crystal orientation between island and film states.

In this study, it was demonstrated that the island-state crystals have increased the degree of {100}-preferred orientation by an increase of the magnetic field. However, the film crystals did not possess distinct preferred orientation by imposition of the field. Reasons for this tendency are considered as follows: The substrate temperature of the present deposition conditions corresponds to 0.48 to $0.54T_m^{Fe}$, at which even bulk diffusion can occur in the solid Fe films. The obtained Fe films were composed of recrystallized grains, as shown in Fig. 6. The films are classified to a zone III film, according to the Structure Zone Model (SZM) [8]. In Fig. 4(a), there are other peaks in the profile (large (110) peaks, etc.). Therefore, a large number of the island crystals are not oriented to <100> direction normal to the substrate. If {100}-oriented island-shaped crystals are coalesced with the other crystals having different orientations, it is inferred that the {100}-oriented crystals decrease their population. In this temperature range, grain growth due to the curvature-driven grain boundary migration occurs during the deposition process. If so, resulted grain structures are not related to the magnetically preferred orientation. As for the driving force of grain boundary migration, it is estimated that the grain boundary energy is larger than the difference in the magnetization energy [9] (or magnetic anisotropy energy, if saturated).

6. Conclusion

Effects of magnetic field imposition of thermal CVD process for Fe deposition were studied and the following conclusions were obtained.

(1) Weight change of $FeCl_3$ source increased as an increase of the imposed magnetic field. Attraction of the chloride gas by the magnetic field was considered for the reason.
(2) The island-state Fe crystals increased their degree of {100} - preferred orientation, however, the film crystals did not possess specific orientation.
(3) Range of substrate temperature for depositing Fe films corresponded to about $T_m^{Fe}/2$. The microstructural evolution process caused reduction of (100)-preferred orientation.

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