Growth, structure and thermal reduction of MOCVD-deposited Fe films on Al₂O₃ (0 0 0 1) substrates

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Abstract

Fe films with strong preferred orientation were prepared on Al₂O₃ (0 0 0 1) substrates by a new two-step method using low-pressure metal-organic chemical vapor deposition (LP-MOCVD) method. X-ray diffraction (XRD) and a vibrating sample magnetometer were employed to characterize the structure and magnetic properties of the Fe films before and after thermal reduction, which was performed in hydrogen flow at 723–1023 K. XRD patterns indicate that the films changed into α-Fe (bcc) mono-phase from a mixture of α-Fe₂O₃ and/or Fe (bcc).

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1. Introduction

The growth of thin magnetic films on semiconductors and insulating substrates has attracted much attention due to the potential for integrating such films into novel semiconductor heterostructure devices [1]. Among them, iron films are subject of intense research work and there are many reports on the epitaxial growth and magnetic properties of Fe films [1–9]. The current research on Fe thin film growth is concentrated on the growth on (0 0 1) GaAs, [1,5,8] Si, [7] SiO₂ [2] and Al₂O₃ [3,4,6] substrates by using magnetron DC and RF sputtering [2], metal-organic chemical vapor deposition (MOCVD) [8,9] and molecular beam epitaxy (MBE) [1,3,4,6]. Transition from super-paramagnetic to ferromagnetic state was reported for ultrathin Fe films prepared by MBE [4]. The magnetic properties of sputtered Fe thin films have been investigated depending on thickness and processing [2], and the magnetic anisotropy behavior [6] was observed in ultrathin Fe films on inclined Al₂O₃ (0 0 0 1) substrates. By now most studies focus on magnetic properties of the Fe thin films, but there have been only few reports on the growth and structure properties of the Fe films. The properties of Fe films are sensitive to the preparation methods and conditions. The film thickness, substrate temperature and deposition pressure have strong effects on the coercivity and saturation magnetization of the Fe films. However, these effects have not been studied clearly.

In this paper, we prepared Fe thin films via a two-step method on Al₂O₃ (0 0 0 1) by using MOCVD, first at 593 K deposition and second at high temperature thermal reduction. We investigated the phase transition of the films by X-ray diffraction (XRD) pattern and analyzed the reaction process.

2. Experiment

The Fe films were grown on (0 0 0 1) sapphire substrates by a LP-MOCVD system with a horizontal rectangular

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quartz reactor. The ironpentacarbonyl ($Fe(CO)_5$) carried by hydrogen was used as Fe source. The source was kept at 278 K during deposition. The sapphire substrates were semi-insulating with (0 0 0 1) orientation. Before loading, they were cleaned by acetone and ethanol for 5 min in an ultrasonic bath and etched in an acid solution ($3H_2SO_4 + 1H_3PO_4$) for 5 min at 433 K, followed by a de-ionized water rinse. The substrates were placed at the center of the graphite boat and inserted in the reactor. Then the growth was performed at 593 K with the pressure ranging from 200 Torr to 500 Torr. After growth, the samples were treated at high temperature in hydrogen atmosphere for 30 min. The typical growth conditions for the Fe films are shown in Table 1.

The structure and composition of the films were studied by XRD spectroscopy before and after thermal reduction. As for magnetic property of the films, M–H curves were measured with a vibrating sample magnetometer (VSM) at room temperature.

3. Result and discussion

The XRD pattern was used to evaluate the crystalline property and the lattice constant of the films. Fig. 1 shows the XRD spectra of three samples grown at 200, 350 and

Table 1
Typical growth conditions for Fe thin film growth on (0 0 0 1) Al_2O_3 substrates

	As-prepared	Thermal reduction
Reactor pressure	200, 350, 500 Torr	Atmospheric pressure
Substrate temperature (K)	593	723–1023
Total H_2 gas flow (l/min)	0.8–1.0	1.6
$Fe(CO)_5$ bubbler flow	12 ml/min	—

500 Torr, respectively. Diffraction peaks at $2\theta \approx 33°$, $49°$ and $68°$ were attributed to (1 0 4), (0 2 4) and (2 0 8) peaks of the Fe_2O_3 compound, respectively, which dominated the XRD spectra. For the samples grown at 200 and 350 Torr, weak (1 1 0) and (2 0 0) diffraction peaks of Fe phase at $2\theta \approx 44.5°$ and $65°$ can be observed. The XRD patterns indicate that all the samples are mainly Fe_2O_3 (hex) polycrystalline films. This is due to the oxidation of Fe and $Fe(CO)_5$ by the oxygen impurity present in the hydrogen. The strong intensities of (1 0 4) and (0 2 4) peaks indicate that the Fe_2O_3 films were not preferentially oriented.

To study the structure behavior after thermal reduction, the samples grown at 350 Torr were annealed under hydrogen atmosphere at temperatures ranging from 723 K to 1023 K. Fig. 2 shows the XRD spectra of the samples after thermal reduction. It can be seen from the XRD patterns that the crystalline composition of the films has been modified after thermal reduction at different temperatures under hydrogen atmosphere. The peak intensity of bcc Fe films increases with increasing annealing temperature from 823 K to 1023 K. Note that the peaks of bcc Fe phase were not observed after annealing at 723 K, and appear again and strengthen with increasing annealing temperature above 823 K. Simultaneously, the Fe_2O_3 phase has disappeared completely. This is due to the competition between the reduction of Fe_2O_3 and the oxidation of Fe with increasing annealing temperature, as depicted by the
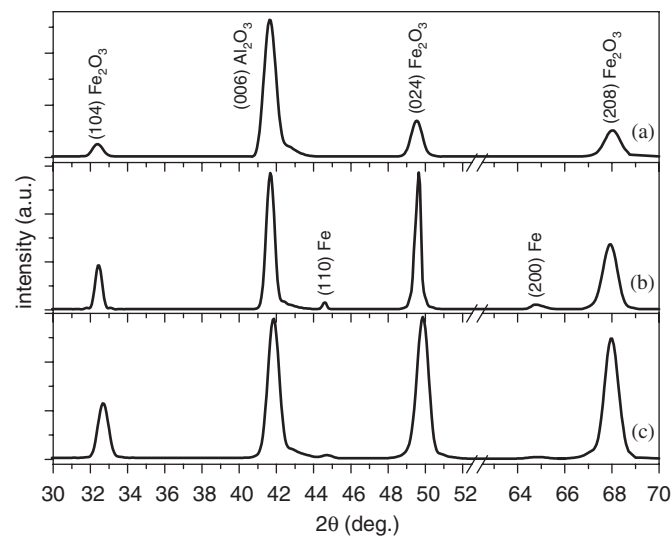

Fig. 1. X-ray diffraction of the as-prepared films with the growth temperature of 593 K: (a) 500 Torr; (b) 350 Torr and (c) 200 Torr.
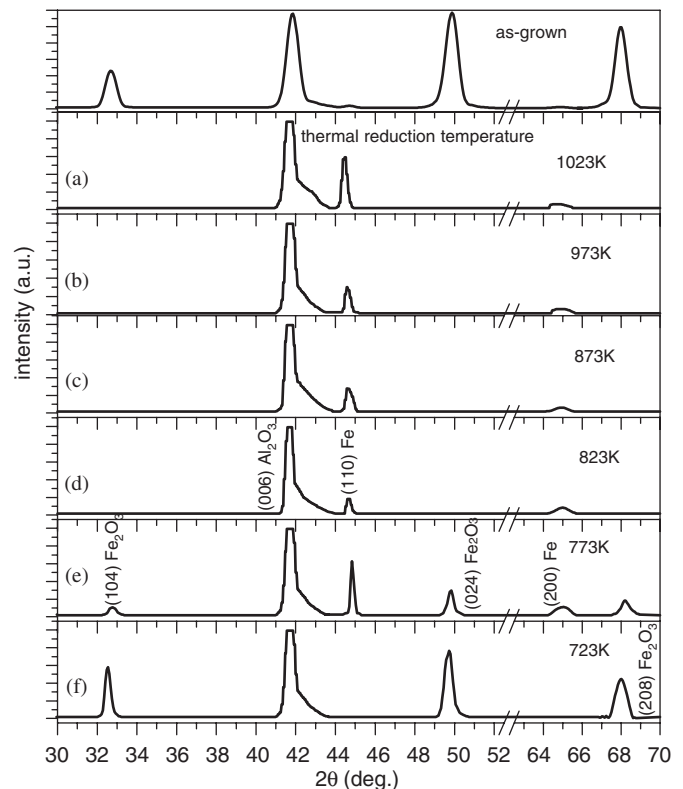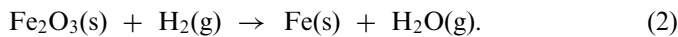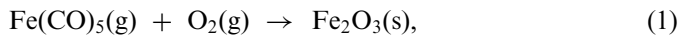

Fig. 2. X-ray diffraction of the films after thermal reduction at different temperatures: (a) 1023 K; (b) 973 K; (c) 873 K; (d) 823 K; (e) 773 K and (f) 723 K, the as-grown films were prepared at 350 Torr.

following reaction equations:

$$Fe(CO)_5(g) + O_2(g) \rightarrow Fe_2O_3(s), \tag{1}$$

$$Fe_2O_3(s) + H_2(g) \rightarrow Fe(s) + H_2O(g). \tag{2}$$

The reactions in the growth chamber are dominated by process (1) at low temperatures, while at high temperatures the reactions are dominated by process (2). From the above analysis, it is obvious that thermal reduction should be carried out at high temperature to obtain Fe.

In Fig. 2, it was found that bcc Fe has preferred orientation of (1 1 0) after thermal reduction. In order to understand the growth process clearly, we show the schematic sketch of structure transition from Fe_2O_3 (hex) phase to Fe (bcc) with preferred orientation of (1 1 0) in Fig. 3. Fig. 3(a) shows the structure of the Fe_2O_3. At high temperature, H_2 is a strong reducer with high chemical activity and it could react with O^{2-} easily as follows:
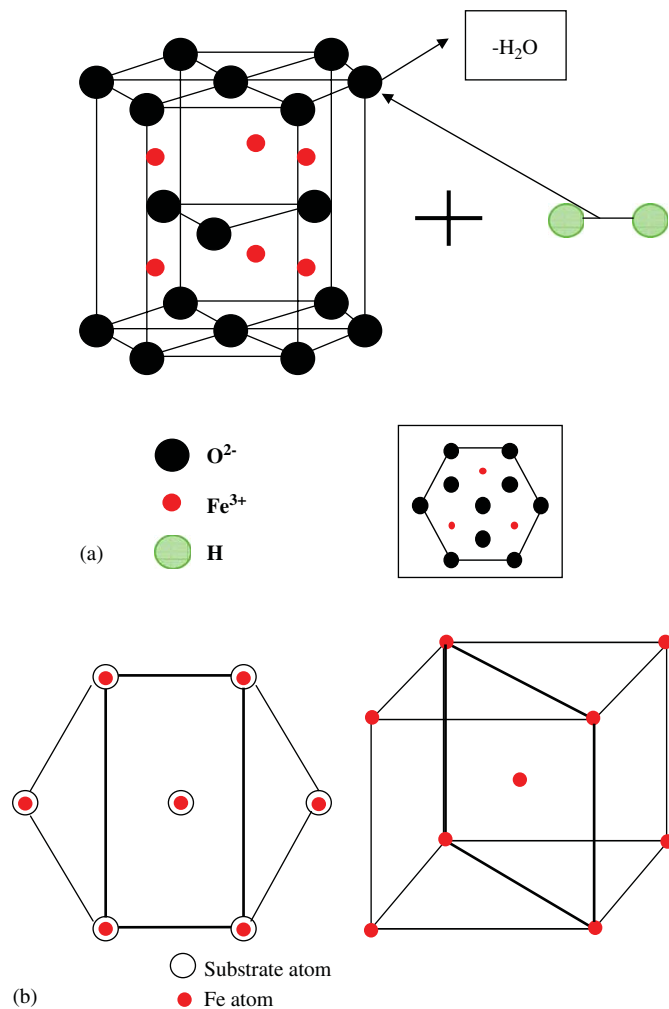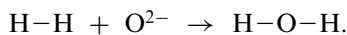
$$H-H + O^{2-} \rightarrow H-O-H.$$

When thermal reduction was carried out, the O^{2-} ions were removed as molecular H_2O by H_2. This epitaxial relationship is shown schematically in Fig. 3(b).

It is well known [11] that the coercivity of soft materials can be exchange coupling with a higher anisotropy material. Bulk α-Fe_2O_3 is known to be antiferromagnetic with low anisotropy. However, early reports revealed a large surface anisotropy in Fe-oxides [10,12]. As shown in Fig. 4, the as-prepared films at 200, 350 and 500 Torr (Fe_2O_3 with small amounts of Fe phase) displayed a ferromagnetic behavior when the direction of the applied magnetic field was perpendicular to the surface of the films. In Fig. 4, the magnetization curve with a coercivity > 240 Oe at room temperature and saturation magnetization (M_s) ~ 5 emu/cm^3 was observed for sample b fabricated at 350 Torr. However, samples a and c show a larger coercivity and smaller M_s than that of sample b. The possible reason could be the presence of an exchange coupling between the Fe phase and the Fe_2O_3. Furthermore, XRD measurements indicate that the film grown at 350 Torr has a maximum intensity of Fe diffraction peaks, which implies that the sample grown at 350 Torr has more Fe phase compared to the other films. Furthermore, the hysteresis loops were also measured with the applied magnetic field parallel to the surface of the films and almost no differences could be

Fig. 3. (a) the structure of Fe_2O_3 (hex) and (b) crystallographic relation between Fe(1 1 0) and Al_2O_3 (0 0 0 1) substrate.
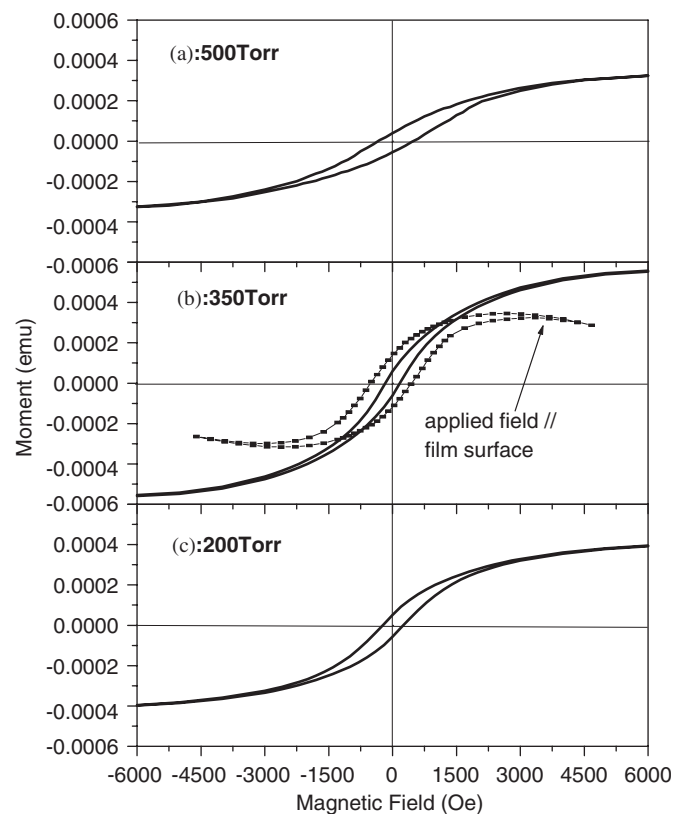

Fig. 4. Magnetization curves for the as-grown films grown at the pressure of (a) 500 Torr; (b) 350 Torr and (c) 200 Torr with the thickness of 1500 nm, the applied magnetic field is perpendicular to the surface of the film. The hysteresis loop of a film prepared at 350 Torr and measured with the applied magnetic field parallel to the surface is also displayed.
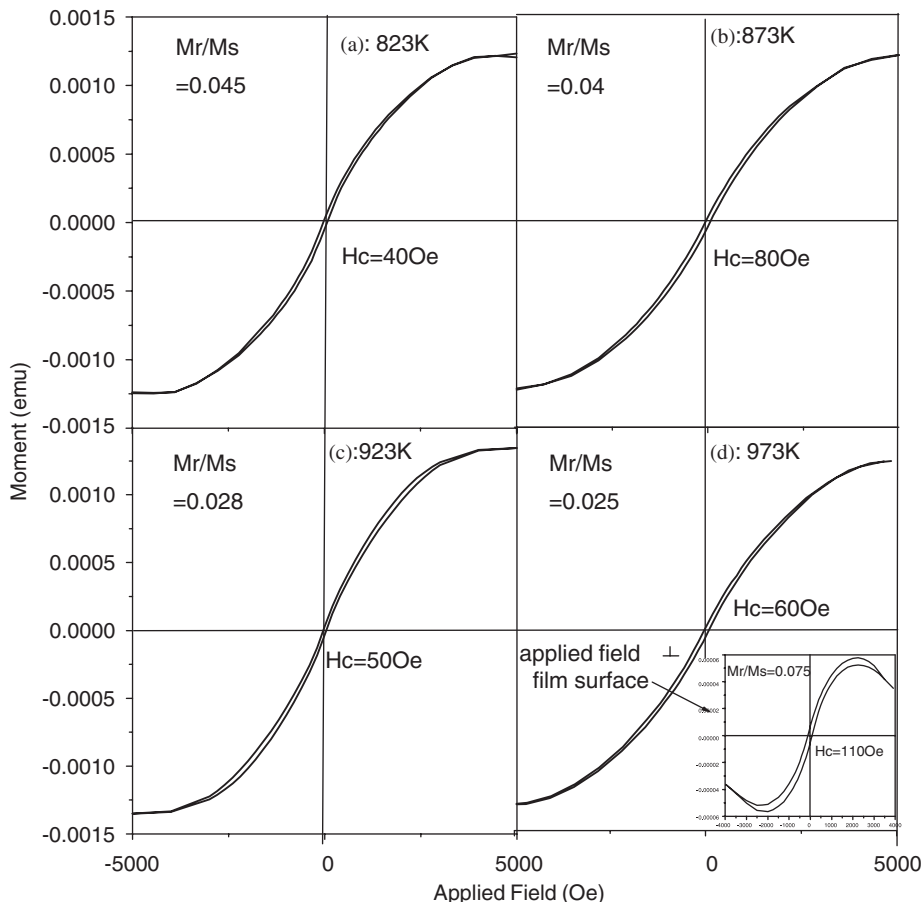
Fig. 5. Magnetization curves for the film after thermal reduction at (a) 823 K; (b) 873 K; (c) 923 K and (d) 973 K with the thickness of 200 nm. The applied magnetic field is parallel to the surface of the substrates. The inset shows the hysteresis loop of a sample annealed at 973 K and measured with the applied magnetic field perpendicular to the surface.

observed between the samples grown at different pressures. A higher coercivity and a slower approach to saturation of in-plane than that of out-of-plane was observed just as shown in Fig. 4(b). Fig. 5 displays a set of magnetization curves of a 200 nm thick Fe film after reduction at different temperatures; the applied magnetic field was parallel to the film surface. All the samples show a decrease in M_r (remanent magnetic)/M_s with increasing annealing temperature. This decrease results from the weakening of the magnetic anisotropy that is due to the roughening of the Fe film surface structure [4]. However, the magnetic properties of the samples are independent of the annealing temperature when the applied magnetic field is perpendicular to the surface of the films. By comparing the in-plane and out-of-plane (see inset of Fig. 5) magnetic properties of the film annealed at 973 K, it can be seen that the in-plane hysteresis loop has lower H_c and M_r/M_s ratio. Meanwhile, it is evident that the coercivity of the Fe films is slightly higher than that of bulk material as shown in Fig. 5. It is well known that the coercivity is determined not only by the microstructure (grain size, porosity, stress) affected by the deposition parameters, but also by the domain wall type [2]. In this work, low-temperature deposition and

high-temperature thermal reduction modify the microstructure of the films. The increase of the coercivity is caused by the growth parameters and the temperature of the thermal reduction is probably the most important parameter.

4. Conclusion

Highly oriented Fe thin films were prepared on Al_2O_3 (0 0 0 1) substrates via a two-step method by using MOCVD. The as-grown films consist of α-Fe_2O_3 and/or Fe (bcc) phase, but after thermal reduction, only α-Fe was detected. This indicates that the α-Fe_2O_3 could be easily transformed into α-Fe phase with preferred orientation by thermal reduction and there are significant differences in coercivity and saturation magnetization between α-Fe and as-prepared films at room temperature.

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