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Evolution from (110) Fe to (111) Fe_3O_4 thin films grown by magnetron sputtering using Fe_2O_3 target

X.J. Wu^a, Z.Z. Zhang^b, Q.S. Liang^a, J. Meng^{a,*}

^a State Key Laboratory of Rare Earth Resources Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun 130022, People's Republic of China

^b State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 3888 Dongnanhu Road, Changchun 130033, People's Republic of China

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1. Introduction

Spintronic devices have shown attractive prospects in many fields such as magnetic storage and quantum computing [1]. Iron (Fe) is an important ferromagnetic metal with a spin polarization of 40%, which is used frequently as spin source in spintronic devices. Tunneling magnetoresistance ratios higher than 1000% has been obtained in Fe-based magnetic tunnel junctions [2]. Electrical control of the magnetic state is also a hot topic. Fe/ BaTiO₃ heterostructure has been studied theoretically and experimentally due to its strong magnetoelectric coupling effects [3,4]. Nowadays, Fe has become an excellent spin source and magnetic material. Amongst Fe oxides, Fe₃O₄ is a ferromagnetic material with half-metallic character. It has shown many advantages for spintronics application, such as high Curie temperature up to 850 K, 100% spin polarization, low electrical resistivity at room temperature and so on [5]. Up to date, thin-film-growth of Fe and Fe₃O₄ has been investigated by many techniques. For mass production, magnetron sputtering is acceptable method that can provide good crystal quality. People have realized Fe and Fe₃O₄ thin films by sputtering, where Fe or Fe₃O₄ target was usually used as the precursor [6]. Magnetic pinching of the plasma would be enhanced by ferromagnetism of Fe targets [7]. Strong magnetic

E-mail address: jmeng@ciac.jl.cn (J. Meng).

ABSTRACT

Fe and Fe₃O₄ thin films were grown by radio frequency magnetron sputtering. Fe₂O₃ was used as the target and hydrogen was introduced together with Argon gas to provide a certain reducing atmosphere. By varying H_2/Ar flow ratio, the changes in composition and structure of the thin films from (110) Fe to (111) Fe₃O₄ were observed by X-ray diffraction. The valence states of Fe in the thin films were analyzed by X-ray photoelectron spectroscopy. Magnetization measurements indicate that the Fe thin films grown with low H_2/Ar flow ratios possess large coercive force. It was ascribed to the increasing boundary density and the increasing amount of Fe oxides such as FeO distributed at the boundary. © 2011 Elsevier B.V. All rights reserved.

field sources and low utilization rate of target would increase the production cost further. For Fe_2O_3 target, a non-magnetic material, it does not have to face the above problems [8]. In this paper, (110) Fe to (111) Fe_3O_4 thin films were fabricated on sapphire substrate by magnetron sputtering with low cost Fe_2O_3 target. The evolutions of the structure and valence states of Fe in the films were studied in detail. Sputtering of Fe and Fe_3O_4 using Fe_2O_3 target may pave the way for mass production of iron based spintronic devices.

2. Experimental

The thin films were fabricated on *c*-plane sapphire substrates. Fe_2O_3 target with 4 N purity was used as the precursor. Ar gas with 5 N purity was used as the sputtering gas. H_2 with 5 N purity was mixed into Ar with variable ratio to provide different reducing atmosphere. The deposition temperature and the chamber pressure were kept at 520 °C and 0.5 Pa, respectively, which were optimized by cross-over experiments. The H_2/Ar flow ratio was changed from 17.6% to 2.3%. The growth was performed for 50 min for all the samples. To protect the thin films against surface oxidation after deposition, an about 3-nm-thick Mg layer was capped on the surface of the thin films by sputtering Mg target in reductive ambient. A dense MgO layer formed in air is expected to have a good protective effect.

^{*} Corresponding author.

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XRD patterns were measured on a Rigaku D/max-RA X-ray diffractometer. The X-ray Photoelectron Spectra (XPS) were measured on an ESCALAB 250 X-ray Photoelectron Spectrometer. A MPMS-XL superconducting quantum interference device (SQUID) was employed to study the magnetic properties of the samples.

3. Results and discussion

Fig. 1 shows the XRD patterns of the thin films grown on *c*-sapphire substrate with different H₂/Ar flow ratios. The samples grown with H₂/Ar flow ratios of 17.6%, 13%, 10%, 7%, 5%, 4%, 3% and 2.3% were labeled as A–H, respectively. To observe clearly all the phases, the diffraction intensity was shown in the logarithm scale. Besides the sapphire (006) peak at 41.68°, a diffraction peak located at about 2θ =44.7° is observed for samples A–D, which is ascribed to the (110) diffractions of Fe. The single Fe (110) peak indicates a good orientation of the thin films.

The full-width at half-maximum (FWHM) of Fe (110) peak are 0.267, 0.258, 0.268 and 0.284 for samples A, B, C and D, corresponding to the grain sizes of 31.9, 33.0, 31.8 and 30.0 nm calculated by Scherrer's equation, respectively.

When the H₂/Ar flow ratio was reduced to 5%, FeO (300) and (310) peaks appear at 20–23°, as shown by the pattern of sample E. By decreasing the H₂/Ar flow ratio to 4%, the FeO (300) and (310) peaks show remarkable increase in intensity. Simultaneously, the Fe (110) diffraction weakens significantly compared to the sapphire (006) peak. Note that three new peaks begin to appear at 2θ =18.2°, 36.9° and 56.8°, which is in accordance with the (111), (222) and (333) peaks of Fe₃O₄ or Fe₂O₃. Because of the similar lattice constants between Fe₃O₄ and γ -Fe₂O₃ (*a*=0.8393 nm for Fe₃O₄ and *a*=0.8351 nm for γ -Fe₂O₃) more accurate identifying needs other characterization tools, such as XPS.

In case of $H_2/Ar=3\%$, the XRD pattern is dominated by (111), (222) and (333) peaks of Fe₃O₄ (or Fe₂O₃). For sample H, which was grown with $H_2/Ar=2.3\%$, diffractions from Fe and FeO

disappear completely from the XRD pattern and only Fe_3O_4 (or Fe_2O_3) peaks are left.

It is well recognized that different Fe oxides (FeO, γ -Fe₂O₃ or Fe₃O₄) can be distinguished from each other by XPS. Fe⁰ has a binding energy of 706.7 eV. FeO (Fe²⁺) has a binding energy of 709.9 eV (with a shake-up satellite peak at 715 eV) and Fe₂O₃ (Fe³⁺) of 711.1 eV (with a shake-up satellite peak at 719.8 eV). The mixed-valence compound Fe₃O₄ has a binding energy ranging from 710.5 to 711.2 eV [9–12].

XPS spectra of samples A–D are shown in Fig. 2(a). Strong Fe^0 2 $P_{3/2}$ peak located at 705.8–706.2 eV indicates that the films are mainly composed of Fe^0 [9]. For sample A, a peak centered at 710.5 eV was observed, corresponding to Fe in oxidation states. For some ferromagnetic metal, surface oxidation will form an antiferromagnetic layer, which influences the magnetic properties significantly. Therefore, a non-magnetic Mg–MgO cap layer with a thickness of 2–3 nm was fabricated to prevent surface oxidation for the other samples. As shown in XPS spectra of samples B–D, signals from surface oxides were not observed any more after adding the Mg–MgO cap layer.

Fig. 2(b) shows the XPS spectra for Fe 2P of samples E to H. Sample E has been confirmed to be a mixture of Fe and FeO by XRD measurements. Correspondingly, both Fe⁰ 2P_{3/2} signal at 706 eV and Fe²⁺ 2P_{3/2} at 709 eV are observed. The satellite peak at about 715 eV for FeO also appears in the spectrum. With decreasing the H₂/Ar ratio to 3%, most Fe 2P signals appear as an envelope ranging from 708 to 712 eV and the Fe⁰ 2P_{3/2} signal at 706 eV becomes very weak, as shown by the XPS of sample G. The above envelope can be fitted into two peaks centered at 709.1 eV and 710.9 eV, which are attributed to Fe²⁺ 2P_{3/2} and Fe³⁺ 2P_{3/2} in Fe₃O₄, respectively [10–12]. Moreover, the satellite peak of Fe²⁺ 2P_{3/2} in FeO was still observed at about 715 eV, indicating the remaining FeO phase. It also agrees with the FeO (310) diffraction in XRD pattern. It should be noted that the satellite peak of Fe₂O₃ Fe³⁺2P_{3/2} at 719 eV does not appear in the spectra, which excludes the existence of Fe₂O₃ phase. Now, it can



Fig. 1. XRD patterns of the thin films deposited on *c*-plane sapphire substrates. The samples grown with H₂/ Ar flow ratios of 17.6%, 13%, 10%, 7%, 5%, 4%, 3% and 2.3% were labeled as A, B, C, D, E, F, G and H, respectively.



Fig. 2. (a) XPS spectra for Fe 2P of samples A–D and (b) XPS spectra for Fe 2P of samples E–H.

be concluded that the XRD peaks at $2\theta = 18.2^{\circ}$, 36.9° and 56.8° are from Fe₃O₄. For the Fe element in Fe₃O₄, one-third exists as Fe²⁺ and the other as Fe³⁺. So the peak area of Fe³⁺ should be larger than that of Fe²⁺. However, the fitting result in Fig. 2(b) shows the contrary case. Considering the remained FeO affirmed by XRD, the larger Fe²⁺ signal intensity should includes the contribution of FeO phase.

With decreasing the H₂/Ar ratio to 2.3%, Fe⁰ 2P_{3/2} peak at 706 eV disappears completely, as exhibited by sample H. In the Fe 2P_{3/2} signals of Fe₃O₄ at 709.1–710.9 eV, the contribution of Fe³⁺ becomes larger than that of Fe²⁺. Near 715 and 719 eV, the positions of Fe²⁺ 2P_{3/2} satellites in FeO and Fe³⁺ 2P_{3/2} satellites in Fe₂O₃, no signal is observed. All above evidences confirm that sample H is pure Fe₃O₄, agreeing with XRD pattern of sample H.

Fig. 3 shows the room temperature magnetic hysteresis loops of samples B, C, D, E, G and H. The magnetic field is parallel to the film plane. For samples B, C, D and E, which are dominated by iron content, the coercive forces are 16, 35, 94 and 220 Oe, respectively. According to the grain size evolvement calculated by XRD result, the increasing boundary density should be responsible for the increasing coercive force partially. More importantly, some Fe oxides may be formed at the boundary as the reduce ambience was degraded, which can provide remarkable pinning effects. As shown by the loop of sample E, which contains a little FeO content characterized by XRD, the coercive force has increased to 220 Oe. For Fe_3O_4 thin films denoted by samples H and G, ferromagnetism has also been observed. Similar to the behavior of Fe series samples, sample G shows a larger coercive force than H. It should be caused by the small amount of FeO content, as confirmed by the XRD result.

4. Conclusions

(110) oriented Fe thin film and (111) oriented Fe₃O₄ thin films were grown on *c*-Al₂O₃ substrates by radio frequency magnetron sputtering. A Fe₂O₃ target was used as the precursor. H₂ was introduced to provide reducing atmosphere. With decreasing the H₂/Ar ratio, the composition of the thin films was changed from Fe to Fe₃O₄ gradually. Fe₂O₃ phase was excluded by the XPS analysis. The thin films dominated by Fe or Fe₃O₄ show ferromagnetism with different coercivity at room temperature. Pinning effects by the increasing boundary density and minute amount of FeO at the boundary are assigned to the main origins for the increasing coercive force.



Fig. 3. Room temperature hysteresis loops of samples B-H under in-plane magnetic field: (a) M-H curves of samples B-E and (b) M-H curves of samples G and H.

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