Growth of highly textured manganese zinc ferrite films on glass substrates

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Highly textured manganese zinc ferrite ($Mn_{0.7}Zn_{0.3}Fe_2O_4$) films have been successfully fabricated on glass substrates by pulse laser deposition at relatively low temperatures. Investigations indicated that the strain, which is induced by high deposition rate and the difference of thermal coefficient between the film and glass substrate, is attributed to the growth of textured structure. Growth of highly textured cobalt ferrite film was also achieved using the same method. This work provided a possible technique for fabricating high quality ferrite films on glass substrates. © *2010 American Institute of Physics*. [doi:10.1063/1.3367964]

I. INTRODUCTION

Manganese-zinc ferrite is a kind of soft magnetic material. For its high permeability, large resistivity, relatively high magnetization, and low coercivity, it has many essential applications such as magnetic sensor, reading head for magnetic recording media, switch mode power supplies, deflection yoke rings, and spintronics devices.[1–5] For the miniaturization of complex geometrical devices, high quality films are required. Ferrite thin films, including manganese zinc ferrite, have been widely investigated.[5–14] Generally, saturation magnetization (M_S) of these ferrite films was much lower than their bulk counterpart. It was probably due to the formation of antiboundary phase and possible disordered phase in the deposited films.[14–17] Epitaxial growth is required to avoid these detrimental factors in order to maintain high M_S. Various methods have been employed for the growth of ferrite films.[12,18,19] However, epitaxial and highly textured growth of ferrite films can only be achieved on single-crystal substrates at relatively high temperatures (>500 °C).[10–12,20]

In this work, we reported a simple technique to control the deposition parameters of manganese zinc ferrite films on glass substrates, thus achieving highly textured films at a very low temperature (268 °C). The strain between the film and glass substrate is attributed to the growth of textured structure. In addition, using the same technique, highly textured $CoFe_2O_4$ film was also successfully fabricated on glass substrate. This work has demonstrated a promising approach for fabricating high quality ferrite films at low temperatures which may pave the way for practical applications and economical mass production.

II. EXPERIMENTAL PROCEDURE

Manganese-zinc-ferrite powders were obtained by a sol-gel combustion method.[21] The powders were pressed into a disk and first sintered at 700 °C for 30 min under 20% O_2 +80% Ar and then at 1000 °C for 1 h under nitrogen atmosphere with a flow rate of 50 SCCM (denotes cubic centimeter per minute at STP). The sintered disk was used as the target. Manganese-zinc ferrite films were deposited on glass substrates using a pulse laser deposition (PLD) system with a base pressure of 2×10^{-8} torr. The deposition power is 7 J/cm^2. In order to avoid oxidation, all of the films were deposited under a vacuum of 10^{-7} torr. The substrate temperature was varied from room temperature to 570 °C. The thicknesses were controlled by the deposition time and measured by a profilometer with a resolution of 0.5 nm. Energy dispersive x-ray spectroscopy and x-ray photoelectron spectroscopy were applied to examine the film composition. The films can be roughly written as $Mn_{0.7}Zn_{0.3}Fe_2O_4$. Transmission electron microscopy (TEM) and x-ray diffraction (XRD) were used for the film characterization and microstructural analysis. Vibrating sample magnetometer was used for the measurement of magnetic properties at room temperature.

III. RESULTS AND DISCUSSION

Figure 1(a) shows XRD spectra of the films deposited at different substrate temperatures. The film thickness is approximately 100 nm. For the film deposited at room temperature, there is no diffraction peak in its XRD spectrum. When the film was deposited at 268 °C, the XRD spectrum shows only one peak (311), suggesting a textured structure of the film. Further increasing the substrate temperature to 418 °C, the film still keeps a textured structure as only (311) and (622) peaks can be observed in the XRD pattern. When the substrate temperature is increased to 570 °C, other indexed peaks, such as (222) and (511) can be clearly seen, suggest-

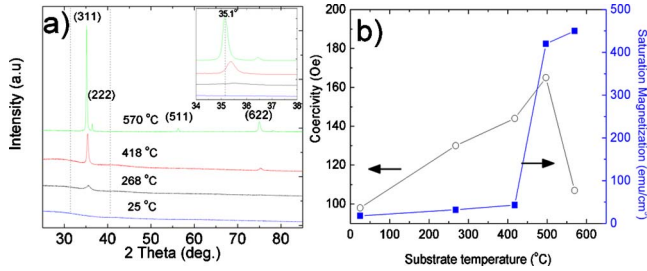a)Electronic mail: mseyj@nus.edu.sg. Tel.: 65-65164097. FAX: 65-68742081.

FIG. 1. (Color online) (a) XRD spectra of manganese zinc ferrite deposited at different temperatures. The inset is the small scale of peak (311); and (b) the saturation magnetization and coercivity dependence on the substrate temperature of the films deposited at different temperatures.

FIG. 3. (Color online) (a) XRD spectra of manganese zinc ferrite films with different thicknesses (substrate temperature 268 °C). The inset is the small scale of peak (311). (b) The dependence of saturation magnetization and coercivity on film thickness (substrate temperature 268 °C). The inset is the hysteresis loop of the film with a thickness of 9 nm (498 °C).

ing that the texture may be deteriorated at this temperature. From the small scale of the main peak (311), a peak shift can be observed for the films deposited at 268 and 418 °C. [The peak (311) is at 35° for the target.] For the film deposited at 570 °C, there is nearly no peak shift. The peak shift in the XRD spectrum is usually due to the strain/stress induced during film growth. Hence, the growth of highly textured structure for the films deposited at 268 and 418 °C may be related to the strain inside films. The strain $\varepsilon_{[hkl]}$ can be estimated by measuring the accurate d-space of the (hkl) plane using XRD: $\varepsilon_{[hkl]} = (d_{[hkl]\text{films}} - d_{[hkl]\text{target}})/d_{[hkl]\text{target}}$.[22] The strain of the films deposited at 268, 418, and 570 °C is thus estimated from Fig. 1(a) to be −1.51%, −0.99%, and −0.29%, respectively. The result reveals that the strain decreases with increasing substrate temperature. The small strain for the film deposited at 570 °C results in a polycrystalline structure.

Magnetic properties of the films deposited at different substrate temperatures are shown in Fig. 1(b). The saturation magnetization (M_S) of the films is relatively low (<100 emu/cm^3) when the deposition temperature is lower than 418 °C. A drastic increase in M_S was found for the film deposited at a substrate temperature of 498 °C. The coercivities of all the films are larger than 100 Oe.

In order to confirm that the film deposited at 268 °C is highly textured, cross-section TEM analysis was performed, as shown in Fig. 2(a). It can be seen that the film is very uniform. No grains can be found from the image, suggesting a single-crystal-like structure. Selecting area electron diffraction (SAED) confirms the single-crystal-like structure of the

film, as shown in the inset of Fig. 2(a) (it should be noted that the film deposited at this temperature may possess some disordered structure, as low M_S is obtained). Figure 2(b) shows in-plane and out-of-plane hysteresis loops of the film deposited at 268 °C. Strong anisotropy can be observed. The easy axis points to in-plane of the film. The in-plane coercivity is approximately 140 Oe while out-of-plane coercivity is only 50 Oe. The angular dependence of coercivity is shown in the inset of Fig. 2(b). The periodical dependence supports the highly textured structure of the film.

Thickness effect on the structural and magnetic properties of the films is shown in Fig. 3. From Fig. 3(a), the diffraction pattern of a 20 nm thick film exhibits only one peak of (311), suggesting a textured structure of the film. The textured structure maintains until the film thickness is more than 100 nm [Fig. 1(a)]. When the film thickness is increased to 160 nm, other diffraction peaks, such as (222), (511), and (444) can be seen, indicating that the texture has strongly deteriorated. From the small scale of the spectra (inset), a blueshift of (311) peak can be observed for all of the films. The strain is estimated to be −2.27%, −2.04%, and −0.4% for the 30, 60, and 160 nm thick films. The result, together with that of the films deposited at different temperatures, indicates that a larger strain results in a better textured structure. Hence, it confirms that the strain is attributed to the growth of highly textured films.

Figure 3(b) shows the magnetic properties of the films with different thicknesses. All of the films show relatively high M_S. The 30 nm film has a M_S of 590 emu/cm^3 higher than bulk (~537 emu/cm^3). High M_S has been found in very thin films of Fe$_3$O$_4$ and NiFe$_2$O$_4$.[23–25] It attributes to cations redistribution. However, the mechanism is still not clear since low M_S due to surface spin disorder or spin canting was also discovered.[13,14] Further investigation is needed to explore this interesting phenomenon.

From Fig. 3(b), the in-plane coercivity increases with increasing film thickness up to 100 nm. The coercivity then slightly decreases with a further increase in thickness. The hysteresis loop of 10 nm film is shown in the inset of Fig. 3(b). The high magnetization and low coercivity of the film may be promising for the applications in high density recording media and spintronics devices.

In order to further investigate the mechanism of the growth of highly textured manganese zinc ferrite films, we deposited the film on a glass substrate at low deposition rate
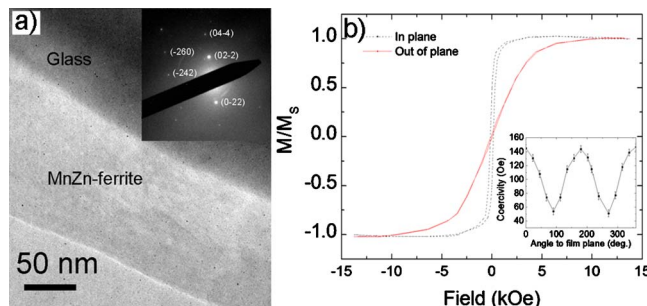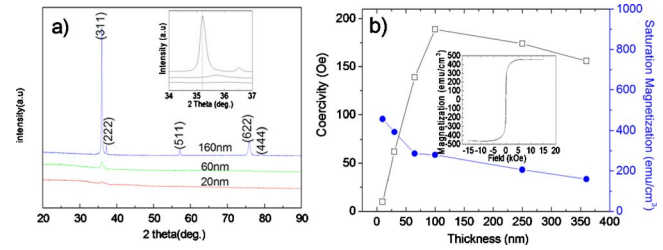

FIG. 2. (Color online) (a) TEM image of manganese zinc ferrite film deposited at 268 °C. The inset is the SAED of the film. (b) In-plane and out of plane of hysteresis loop of manganese zinc ferrite film deposited at 268 °C with a thickness of 60 nm. The inset is the angular dependence of coercivity.
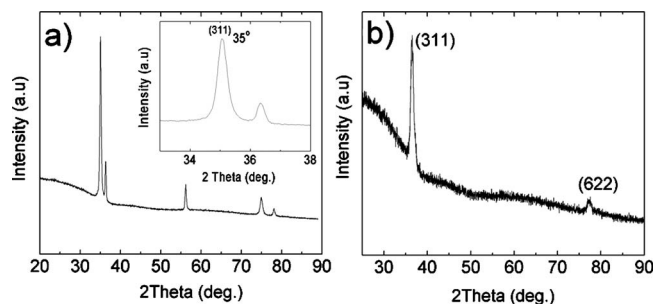
FIG. 4. (a) XRD spectrum of manganese zinc ferrite film deposited with a very low deposition rate (0.5 nm/min). The inset is the small scale of peak (311). (b) XRD spectrum of cobalt ferrite film deposited at 418 °C with a deposition rate of 10 nm/min with a thickness of 60 nm (10^{-4} torr O_2)

(0.5 nm/min at 0.35 J/cm^2). The XRD spectrum of the film is shown in Fig. 4(a). There is nearly no textured structure of the film. The inset shows the small scale of the diffraction peak (311). It indicates that peak (311) is in the position of 35°, the same as that of the target, suggesting that there may be no strain/stress. The result confirms that the strain in the film plays an important role in the growth of the textured structure. It should be noted that the highly textured structure in the orientation of (311) remains at a deposition rate higher than 10 nm/min.

It is known that for a PLD process, the ablation temperature is much lower than the melting temperature of a target. The film growth is far from equilibrium and the ablated atoms do not have enough mobility to achieve the lowest thermal dynamic energy state. Hence, strain may be induced during the film growth. When the film was deposited at the low temperature and high deposition rate, a large strain could be induced in the interface between the film and glass substrate. In addition, the difference of thermal coefficient between the film and glass substrate may also induce strain/stress during film growth.[26] The minimization of strain energy density leads to the formation of (311) texture. For the film grown at high temperatures, the high diffusion rate of the ablated atoms may reduce the strain, leading to an isotropic growth of the film [Fig. 1(a)], and therefore the film is polycrystalline. Similarly, for the film grown at a low deposition rate, the ablated atoms may also have enough mobility toward their lowest energy state. A polycrystalline structure of the film is thus formed. For the very thick film as described in Fig. 3(a), the strain is easily relaxed since the strain is induced at the interface. Hence, the textured structure cannot be formed.

The strain inside the film prepared by PLD can be induced by shot-peening effects, which is generated by the impingement of energetic particles on the already grown film.[27] However, in this work, the investigation on the effect of thickness and deposition rate has shown that for the films with large thickness and grown with a very low deposition rate, there is no peak shift in the XRD spectra, suggesting no or low strain. Therefore, the strain induced by shot-peening effect is not likely the key factor for the growth of highly textured films.

Since the strain is induced only by relatively high laser fluences, it can be used to fabricate other high quality films

on glass substrates. We have deposited cobalt ferrite films as an example. When cobalt ferrite was deposited on a glass substrate at a substrate temperature of 418 °C and a deposition rate of 10 nm/min (10^{-4} torr O_2), the film shows highly textured structure [Fig. 4(b)]. It suggests that this method may be employed as a universal approach to grow high quality oxide films on glass substrates.

In conclusion, we report that highly textured manganese zinc-ferrite films have been successfully fabricated on glass substrates due to the strain induced during film growth. The textured film has a high saturation magnetization and relatively low coercivity. Textured cobalt ferrite films on glass substrates were also achieved using the same method. This work may provide a simple approach to produce high quality films on cheap substrates (i.e., glass).

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