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Growth of crystalline cobalt ferrite thin films at lower temperatures using pulsed-laser deposition technique

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Cobalt ferrite thin films were grown on SiO_2/Si(100) substrates using pulsed-laser deposition technique at substrate temperatures ranging from 250 to 600 °C. Thermal expansion mismatch between the film and substrate appears to have a substantial effect on the magnetic properties of the cobalt ferrite films, due to the large magnetoelastic coupling of cobalt ferrite. It was shown in this study, that polycrystalline films with (111)-preferred orientation could be prepared at substrate temperatures as low as 250 °C. The growth of crystalline cobalt ferrite films at such low temperatures indicates the potential to use cobalt ferrite for microelectromechanical systems devices and sensor applications including integration with a wider range of multilayer device structures.
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I. INTRODUCTION

Due to exceptional magnetoelastic, magnetotransport, magnetooptical, photomagnetic, electronic, and magnetic properties, cobalt ferrite (CFO) has been proposed for applications in noncontact force and torque sensors,[1] as spin filters for magnetic tunnel junctions,[2] for hybrid data storage,[3] for magnetooptical media,[4] and as anode materials for advanced Li-ion batteries.[5] Depending on the requirements of application, magnetic and magnetoelastic properties of CFO can be fine-tuned by appropriate cation substitution[1,6–8] and magnetic annealing.[9]

The optimum substrate temperature for thin film growth has been reported to be 600 °C,[10] in order to produce crystalline CFO. However, such high substrate temperatures limit the potential use of CFO in microelectromechanical systems (MEMS) devices, multilayer hybrid sensors, or integration with giant magnetoresistance, tunneling magnetoresistance, or semiconductor devices. Hence, it is necessary to investigate the optimum growth conditions for CFOs, which would enable pulsed-laser deposition (PLD) of crystalline CFO films at lower substrate temperatures.

II. THIN FILM GROWTH

The films for this study were deposited from a $CoFe_2O_4$ target using a 248 nm KrF excimer laser at 210 mJ and 13 Hz repetition rate. The laser spot size was 9×1.5 mm^2. The target-to-substrate distance was maintained at 5 cm. Substrates were Si(100) wafers with 300 nm thermal SiO_2 on top. The chamber was pumped down to 1×10^{-7} Torr before deposition. A series of five different substrate temperatures (T_{DEP}) were investigated: 250, 350, 450, 550, and 600 °C. All films were deposited in 22 mTorr of oxygen, and cooled to room temperature under the same oxygen pressure. This process gave film growth rates of 2.25 nm/min, which did not vary with deposition temperature in this study.

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III. EXPERIMENTAL

Film thicknesses were measured from cross-sections in the scanning electron microscope (SEM), and were 135 ± 5 nm for all samples. Crystal structure and orientation were investigated by θ-2θ x-ray diffraction (XRD) scans. Composition was determined by energy-dispersive x-ray spectroscopy (EDX) in the SEM, averaging over 15 locations. Magnetic hysteresis loops were measured at room temperature using a vibrating sample magnetometer (VSM) with maximum applied field of 16 kOe.

Surface morphology and roughness of the deposited films were determined by atomic force microscopy (AFM). The imaging of magnetic domains in the films was carried out using magnetic force microscopy (MFM) with the phase detection technique.

IV. RESULTS AND DISCUSSION

A. Crystallography

The XRD patterns of the deposited CFO films are shown in Fig. 1. All of the films were crystalline and single-phase with the cubic spinel structure. From EDX, compositions were found to be $Co_{1.1}Fe_{1.9}O_4$ (with the oxygen content assumed, since EDX cannot determine it accurately). The films grown at low T_{DEP} showed preferred (111)-texture with some (311) whereas, at higher temperatures, films prefer to grow in (100) and (311) orientation. This represents a considerably different trend from that observed by Zhou *et al.*[10] The growth of crystalline CFO films with (111)-texture at lower temperatures (T_{DEP}=250 °C) show potential for hybrid multilayer sensor applications and integration with multilayer structures that require lower processing temperatures.

B. Magnetic properties

Hysteresis loops of the CFO films, measured by VSM at room temperature are shown in Figs. 2(a)–2(e). The films deposited at 600 °C and 550 °C show a large perpendicular

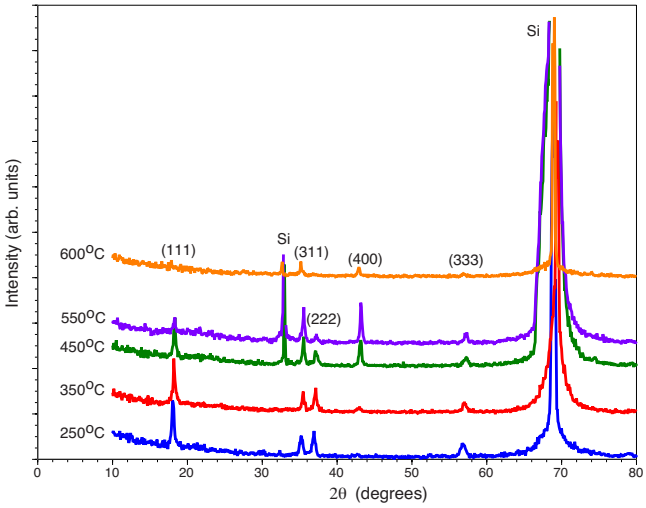

FIG. 1. (Color online) XRD patterns of films deposited at different substrate temperatures. At lower temperatures, the films were crystalline with predominantly (111)-texture and some (311) whereas, at higher temperatures, preferred orientation is (100) and (311).

anisotropy contribution [see Figs. 2(a) and 2(b)]. For decreasing T_{DEP}, the hysteresis loops show the perpendicular anisotropy contribution decreasing, and the in-plane anisotropy contribution increasing [Figs. 2(c)–2(e)]. However, although the effect of perpendicular anisotropy contribution is less significant at lower temperatures, it is still high enough to produce substantial out-of-plane magnetization [Figs. 3(a)–3(e)], and contribute to the high coercivity of the films.

It is evident from Fig. 2(f) that in-plane coercivity is almost constant with temperature whereas the coercivity measured from perpendicular loops increases with temperature indicating also that the perpendicular magnetic anisotropy increases with T_{DEP}.

The thermal expansion coefficients of silicon substrate and CFO are reported to be 3.5×10^{-6} K^{-1} and 1×10^{-5} K^{-1}, respectively.[10] Due to the mismatch, when the substrate-film combination is cooled down to room temperature, an in-plane isotropic tension will be induced in the film. The amount of strain induced due to thermal expansion mismatch can be predicted from[11]

$$\varepsilon = (\alpha_s - \alpha_f)\Delta T, \tag{1}$$

where α_s and α_f are thermal expansion coefficients of substrate and film, respectively, and ΔT is the difference between the deposition temperature and measuring temperature (usually room temperature). Figure 2(g) shows the predicted induced strain due to thermal expansion mismatch versus substrate temperature. As the T_{DEP} increases, strain induced on the film becomes larger showing a linear relationship. Since CFO has predominantly negative magnetostriction,[9] in-plane tension is expected to give rise to perpendicular magnetic anisotropy, which increases with increasing T_{DEP}.

Crystallographic texture together with magnetocrystalline anisotropy can also contribute to perpendicular anisotropy. To the extent that the high T_{DEP} films show some preferred (100)-texture, that would be expected to contribute some in-plane anisotropy (since K_1 is reported to be positive for CFO[12]) and to the extent that the lower T_{DEP} films show some preferred (111)-texture, that would be expected to contribute some perpendicular anisotropy.[13] However for the films of this study, it is apparent that the magnetoelastic contribution predominates, since the perpendicular anisotropy shows the reverse trend (highest for highest T_{DEP} and lowest for lower T_{DEP}).

The variation in magnetization (measured at 16 kOe applied field) with T_{DEP} is shown in Fig. 2(h). As the T_{DEP} increases, magnetization increases probably due to varying amounts of oxygen vacancies and varying cation site occupancies of Co and Fe. At 600 °C, the magnetization decreases by 10% from its peak value. As can be seen from Fig. 2(h), the room temperature magnetization values (measured at 16 kOe) lie in the range of 130–270 emu/cm^3 whereas the saturation magnetization value of bulk CFO is ~400 emu/cm^3.[14]

C. Surface morphology and domain imaging

Figures 3(a)–3(e) show surface morphology seen in AFM (on the left) and magnetic domain patterns seen in MFM (on the right) of CFO thin films deposited at different temperatures. The rms surface roughness was found to be

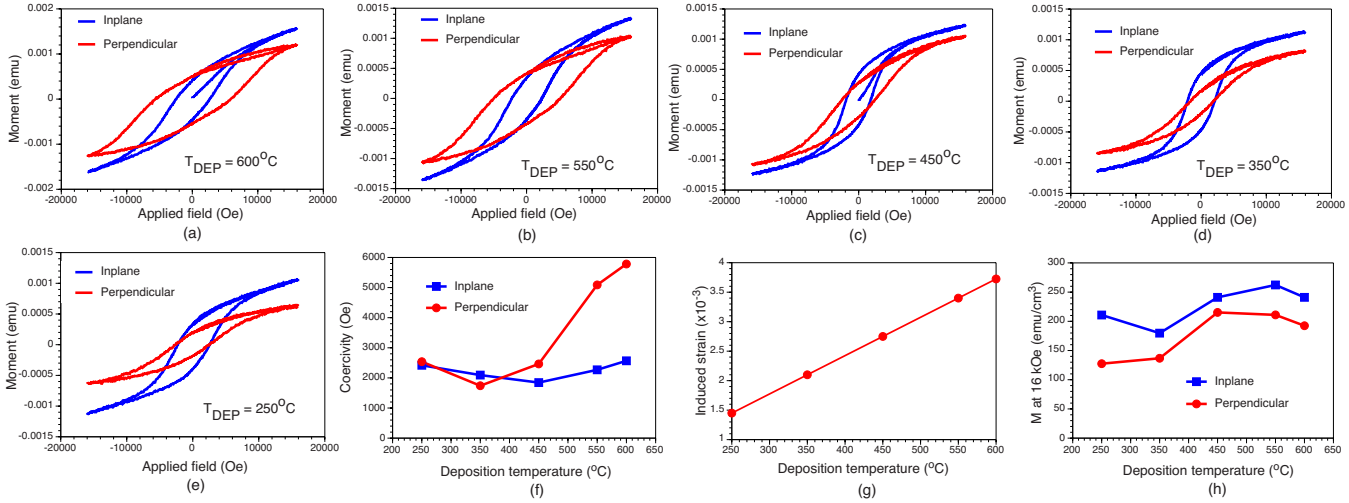

FIG. 2. (Color online) (a)–(e) M-H hysteresis loops of CFO thin films deposited at 600 °C, 550 °C, 450 °C, 350 °C, and 250 °C, respectively. (f) Coercivity as a function of substrate temperature. (g) Calculated variation in thermal expansion mismatch-induced strain with deposition temperature. (h) Variation in measured magnetization (at 16 kOe) with deposition temperature.

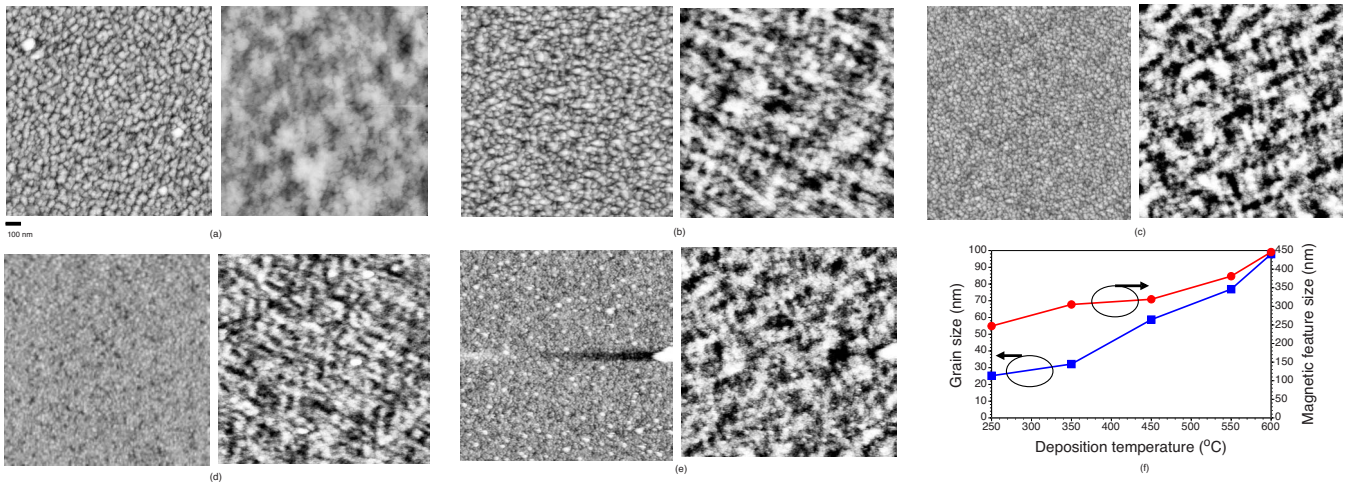

FIG. 3. (Color online) (a)–(e) AFM (left) and MFM (right) images of CFO samples deposited at 600 °C, 550 °C, 450 °C, 350 °C, and 250 °C, respectively. The grain size and magnetic feature size increase with deposition temperature and are plotted in (f). Magnetic domains are irregular in shape but reflect a feature size similar to the equilibrium period of maze type domains. This type of behavior is typical for magnetic thin films with high perpendicular anisotropy and high domain wall coercivity Ref. 15.

around 3 nm for all samples. The grain size increases with T_{DEP} as shown in Fig. 3(f) from about 25 nm for T_{DEP} =250 °C, to about 100 nm for T_{DEP}=600 °C.

Irregular domain patterns with global nonequilibrium character observed in these films are commonly observed in materials with strong perpendicular anisotropy and high domain wall coercivity. Though these domains are at global nonequilibrium, they nonetheless reflect a typical feature size similar to the equilibrium period of maze-type domains.[15] As shown in Fig. 3(f), the magnetic feature size increases with increasing T_{DEP}. According to a simple stripe domain model, for materials with easy axis perpendicular to the crystal surface, the domain width (or magnetic feature size) increases with increasing perpendicular anisotropy constant K_u (as $K_u^{1/4}$).[16] Hence the observed increase in magnetic domain size is consistent with the magnetic property measurements discussed in Sec. IV B, where perpendicular anisotropy was also observed to increase with increasing T_{DEP}.

Grain size and magnetic feature size increase with T_{DEP} at different rates. In films deposited at 250 °C each magnetic domain is made up of approximately 100 grains, whereas for films deposited at 600 °C, each magnetic domain is made up of about 25 grains.

V. CONCLUSIONS

CFO thin films were grown on SiO_2/Si(100) substrates using the PLD technique, at a series of deposition temperatures, ranging from 250 to 600 °C. It was shown in this study that crystalline CFO thin films with (111)-preferred orientation can be grown at temperatures as low as 250 °C, as opposed to the optimum value of 600 °C reported in the literature.[10] The films were observed to have a substantial perpendicular magnetic anisotropy, which decreased with decreasing substrate temperature. The variation in perpendicular anisotropy and coercivity with substrate temperature are believed to be predominantly due to the thermal expansion mismatch between the film and the substrate. The growth of CFO thin films at lower temperatures indicates their potential to be integrated with a wider range of multilayer device structures and MEMS devices.

The saturation magnetization in such CFO thin films could be further improved by optimizing deposition oxygen pressure or by postdeposition annealing in an oxygen-containing atmosphere, in order to decrease oxygen vacancies.

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