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Role of crystal orientation on the magnetic properties of $CoFe_2O_4$ thin films grown on Si (1 0 0) and Al_2O_3 (0 0 0 1) substrates using pulsed laser deposition

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ABSTRACT

We report the influence of crystal orientation on the magnetic properties of $CoFe_2O_4$ (CFO) thin films grown on single crystal Si (1 0 0) and c-cut sapphire (Al_2O_3) (0 0 0 1) substrates using pulsed laser deposition technique. The thickness was varied from 200 to 50 nm for CFO films grown on Si substrates, while it was fixed at 200 nm for CFO films grown on Al_2O_3 substrates. We observed that the 200 and 100 nm thick CFO–Si films grew in both (1 1 1) and (3 1 1) directions and displayed out-of-plane anisotropy, whereas the 50 nm thick CFO–Si film showed only an (1 1 1) orientation and an in-plane anisotropy. The 200 nm thick CFO film grown on an Al_2O_3 substrate was also found to show a complete (1 1 1) orientation and a strong in-plane anisotropy. These observations pointed to a definite relation between the crystalline orientation and the observed magnetic anisotropy in the CFO thin films.

1. Introduction

$CoFe_2O_4$ (CFO) possesses an inverse spinel structure in that 8 tetrahedral cation sites are occupied by eight Fe^{3+} ions whereas the 16 octahedral cation sites are randomly occupied by eight Co^{2+} and eight Fe^{3+} ions [1]. A unit cell of CFO consists of 8 formula units and has a face-centered-cubic (fcc) structure with lattice parameter (a_o) of 8.39 Å. CFO films with large coercivity, large permeability at high frequency, large magnetocrystalline anisotropy and magnetostriction, high chemical and mechanical stabilities and relatively low conductivity are technologically important materials for a wide range of applications, such as in microwave devices, magnetostrictive sensors, biomolecular drug delivery and electronic devices [2–10]. Due to a coupling between the high magnetostriction and large magnetocrystalline anisotropy [11], CFO has recently been combined with ferroelectric materials, such as $BaTiO_3$ (BTO), $PbTiO_3$ (PTO) and $Pb(Zr,Ti)O_3$ (PZT), to make multiferroic materials for potential use in electric-field-controlled magnetic data storage and magnetically tunable dielectrics [12–18]. Evidence of strong magnetoelastic coupling has been observed in a vertically self-assembled CFO–BTO nanostructure around its ferroelectric Curie temperature [12]. It has been shown that it is the strain-mediated magnetoelastic coupling between BTO and CFO that induces magnetic reversal [14]. The high values of dielectric constant and nonlinear dielectric signal, along with tunable magnetic properties, have been reported on CFO–PTO nanocomposites [13]. Magnetoelectric (ME) coupling and influence of ferromagnetic/ferroelectric layer thickness on the ME coupling have been studied in CFO–PZT bilayer and PZT/CFO/PZT trilayer films [18–20]. Sim et al. [19] reported the enhancement of saturation magnetization in CFO–PZT bilayer films as the PZT film thickness was increased. Ferroelectric and dielectric measurements also revealed that the presence of an interfacial space charge polarization arose mainly from the ferroelectric/magnetic interface, and the largest values of ferroelectric parameters were achieved in films with optimized thickness of PZT. However, Lin et al. [20] reported that the ferroelectric properties of PZT/CFO/PZT films remained almost unchanged as the CFO film thickness varied from 120 to 40 nm, as a result of the lower resistance of the CFO layer in the PZT/CFO/PZT trilayer configuration. Despite these studies, the mechanism and influence of magnetic layer thickness on the ME coupling in CFO-based multiferroic films have remained elusive [18–21].

In this context, we believe that a clear understanding of the relationship between the crystalline growth and magnetic properties in CFO thin films upon film thickness variation is of critical importance. In this work a comparative study of the structure and magnetic properties of CFO films of three different thicknesses (t=200, 100 and 50 nm) that were grown on Si (1 0 0) substrates is presented. The CFO films of 200 nm thickness were also grown on Al_2O_3 (0 0 0 1) substrates for the purpose of comparison. We observed that the 200 and 100 nm thick CFO–Si films possessed

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both (3 1 1) and (1 1 1) orientations and exhibited out-of-plane anisotropy, whereas the 50 nm thick CFO–Si film showed only a (1 1 1) texture and an in-plane anisotropy. The CFO film grown on a c-cut Al_2O_3 substrate was also found to possess only a (1 1 1) texture and an in-plane anisotropy. These observations pointed to the importance of the crystalline orientation on the observed magnetic anisotropy in the CFO thin films.

2. Experimental

Cobalt ferrite (CFO) thin films of different thicknesses were grown on single crystal Si (1 0 0) and c-cut sapphire (Al_2O_3) substrates using pulsed laser deposition (PLD) technique. A KrF excimer laser (λ=248 nm) operating at 10 Hz was used to ablate the CFO target. The energy density or fluence at the target surface was maintained at 2 J/cm^2 during ablation. The CFO target was prepared by standard pressing–sintering technique using high purity CFO powder. All the thin films were deposited at a substrate temperature of 450 °C under a background O_2 pressure of 10 mT. Under these growth conditions, the average deposition rate for the films was measured to be 0.1 Å/pulse. A distance of 6 cm was maintained between the substrates and the targets during deposition. The crystallinity and orientation of the as-deposited films were determined by conventional θ–2θ X-ray diffraction (XRD) method using a Bruker D8 Focus Diffractometer. Care was taken to avoid peak shifts in the XRD patterns due to sample misalignment while performing the XRD scans. The surface morphologies of the films were studied using an Atomic Force Microscope (AFM) from Digital Instruments. The magnetic properties were measured for both the in-plane and out-of-plane configurations of the films in magnetic fields up to 50 kOe using a commercial Physical Property Measurement System (PPMS) from Quantum Design.

3. Results and discussion

Fig. 1 shows the XRD θ–2θ scans of CFO films grown on Si substrates under the same conditions for different thicknesses of 200, 100 and 50 nm, respectively. The XRD pattern of the 200 nm thick film demonstrates a bulk-like polycrystalline nature (Fig. 1a). The observed peaks are indexed to the face-centered cubic phase of CFO with a space group of Fd-3m (2 2 7) and lattice parameter a=8.391 Å. While the (1 1 1) peak was present in all films investigated, the intensity of the (3 1 1) peak strongly varied with film thickness. It can be seen that the (3 1 1) peak of high intensity was observed for the 200 nm thick film (Fig. 1a), which became largely suppressed for the 100 nm thick film (Fig. 1b) and disappeared for the 50 nm thick film (Fig. 1c). Clearly, the XRD pattern of the 50 nm thick film showed a complete (1 1 1) texture (Fig. 1c). This could be reconciled from the perspective that below a critical film thickness, the (1 1 1) orientation was the preferred growth direction for CFO–Si thin films [9,22].

To better understand this, CFO films of 200 nm thickness were grown on c-cut sapphire or Al_2O_3 (0 0 0 1) substrates for comparison. As one can see clearly in Fig. 2, the XRD θ–2θ scan of this sample showed a strong (1 1 1) texture with no additional (3 1 1) orientations of CFO. This is consistent with previous observations that showed that spinel-type ferrite thin films grew with a strong (1 1 1) orientation on Al_2O_3 substrates [23,24]. The hexagonal surface unit cells of an Al_2O_3 substrate could actually provide triangular lattice nucleation sites for the CFO (1 1 1) plane. This gave a small lattice mismatch of 2.8% between CFO and Al_2O_3 along the (1 1 1) direction. Our results presented here clearly indicate that the crystal orientation in CFO films can change depending upon film thickness and/or substrate used.

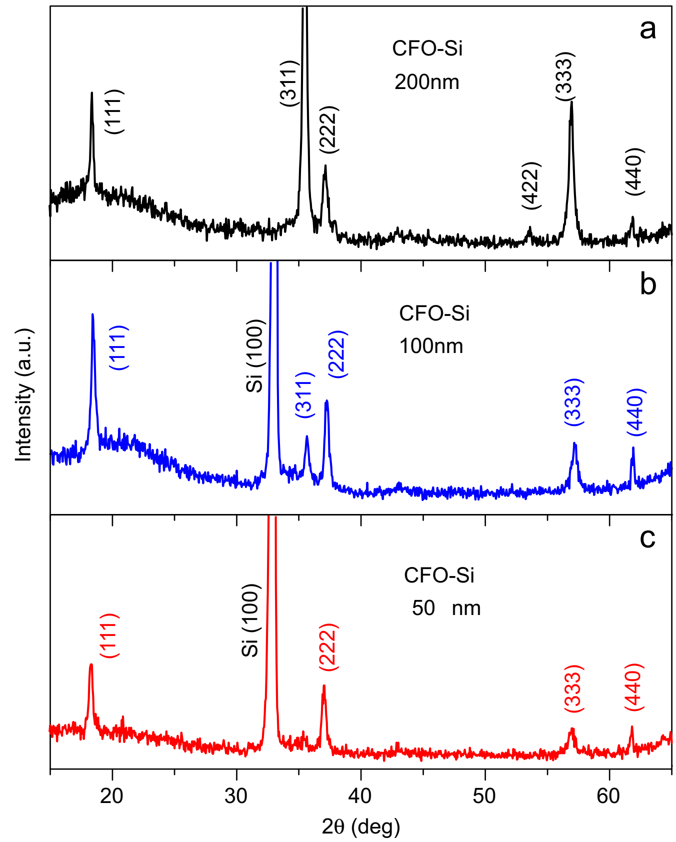

Fig. 1. XRD patterns for (a) 200 nm, (b) 100 nm and (c) 50 nm thick films of CFO grown on Si (1 0 0) substrates, respectively.

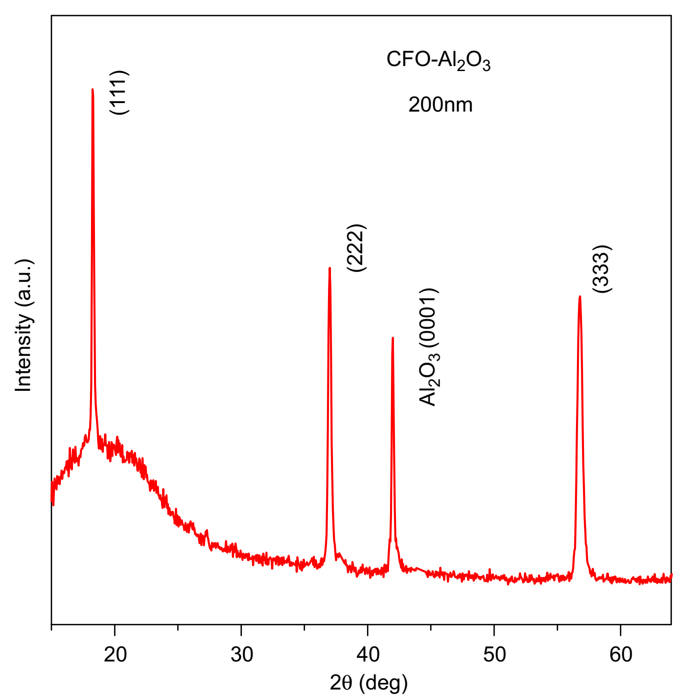

Fig. 2. XRD θ–2θ scan of the 200 nm thick CFO film grown on an Al_2O_3 (0 0 0 1) substrate.

From the broadening of the XRD peaks shown in Fig. 1, the average crystallite sizes (D) in the CFO films were calculated using