TUNING THE MAGNETOELECTRIC PROPERTIES WITH STRAIN IN EPITAXIAL $CO_{0.9}SN_{0.1}FE_2O_4$ THIN FILMS

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Abstract

We have grown epitaxial Sn substituted cobalt ferrite thin films of various thicknesses on piezoelectric $Pb(Mg_{1/3}Nb_{2/3})_{0.72}Ti_{0.28}O_3$ substrates and investigated the strain-induced changes of magnetic properties. All films described in this work have been deposited by pulsed laser deposition (PLD) from stoichiometric target of $Co_{0.9}Sn_{0.1}Fe_2O_4$.The lattice structure, crystallinity and orientation of the thin films were determined by X-ray diffraction analysis. The magnetization of thin films was measured for both, in-plane and out-of-plane configurations, using a superconductor quantum interference device (SQUID) magnetometer at 300 K. The measurements reveal that the magnetic anisotropy is altered by the strain imposed from the substrate upon application of an electric field. The magnetoelastic coupling is demonstrated by a change of the remanent magnetisation. However, we find that this strain effect is thickness dependent. The biggest strain effect is recorded for the thickest film (400nm) where an electric-field-controlled contraction of the substrate of 0.1% induces a relative change in magnetic moment of 9.3%. The relative change of the remanent magnetisation is reduced with decreasing film thickness and is smaller than 3% for the thinnest film (25nm).

Keywords: Ferrite, substitution, magnetoelectric, magnetism, epitaxy

1. INTRODUCTION

The magnetic properties of cobalt ferritecan be modified by ion substitution and adding proper substitution elements, such as Ni, Mn, Cd, Sn [1, 2]. The substitution with different elements allows the variation in ferrites properties that can be tuned to specific applications for high-density magnetic recording [3], ferrofluids technology [4], biomedical drug delivery and biocompatible magnetic nanoparticles for cancer treatment [5], magnetic resonance imaging [6] and magneto-optical devices. This study focuses on the structure and magnetic properties of $Co_{0.9}Sn_{0.1}Fe_2O_4$ (CSFO) cobalt ferrite thin films [7]. There are few reports on the influence of Sn substitution on the structure, microstructure and magnetic properties of the ferrite thin films. Sn^{+4} was used as a substitution element [8] in order to prove that the substitution of Sn^{+4} ions in manganese-zinc ferrite can influence the temperature dependence of initial permeability and total power loss. Recently, ferrite were doped with SnO_2 in order to obtain fine granules of MnZn ferrite with low-loss [9, 10] also to demonstrate the functionality of the humidity sensor [11]. Moreover, Sn substituted Zn ferrite was investigated by Das *et al.* [12] in order to improve the microstructure and the magnetic properties. The magnetic properties of ferrites such as permeability, magnetization, coercive field and Curie temperature are affected by composition as well as by the type of substitution, cation distribution and obtaining method [13]. In this work, we deposited CSFO thin films of three thickness on $0.72Pb(Mg_{1/3}Nb_{2/3})O_3–0.28PbTiO_3$ (PMN-PT) single-crystal substrates and present a further study of the effect of substrate induced lattice strain in CSFO by PMN-PT via the converse piezoelectric effect. A voltage U=350V has been applied to the PMN-PT during SQUID measurement to record the strain-induced change of anisotropy of the films. A biaxial in-plane compression of 0.1% at E = 10 kV/cm has been reported when a voltage of U<350 V is applied along substrate normal [14]. Ferrolectric $Pb(Mg_{1/3}Nb_{2/3})_{1−x}Ti_xO_3$ single crystals provide ultrahigh piezoelectric coefficients and are widely used as substrates [15]. The magneto electric coupling mainly results from the magnetic-mechanical-electric interaction through the stress and/or strain transforming from one subsystem to another [16].

2. MAIN TEXT EXPERIMENTAL

A series of CSFO films grown on PMN-PT substrate are studied. CSFO films have been grown with distinct thickness varying from 50 to 400 nm on the (001) orientated substrates in order to analyze the effect of thickness dependent on magnetic properties. The laser beam was focused by optical lenses at an angle of about 45 deg to the rotating target and the substrate was placed at a distance of 4 cm to the target. Before deposition, the chamber was evacuated to 0.05 mbar. The films were deposited at a substrate temperature of 650 °C. After deposition, the films were annealed for 15 min and cooled down to room temperature at an oxygen pressure of about 0.5 bar. The crystallinity and orientation of the thin films were determined by X-ray diffraction (XRD) analysis using ω −2θ scans, φ-scans, and ω-scans (rocking curves) which were performed by Cu radiation (wavelength of 0.154017 nm) using an Panalytical X'Pert MRD diffractometer. The film thickness was determined *ex-situ* by means of X-ray reflectivity (XRR) measurements for films up to 80 nm. For the thicker films the XRR cannot provide further information due to the limited instrumental resolution of the diffractometer and the substrate topography. The thickness of these films was estimated by pulse number. Before each XRD analysis, the sample alignment was performed on the PMN-PT(002) peak of the substrate in order to avoid the peak shift due to the sample misalignment. The magnetization of thin films was measured for both in-plane (magnetic field applied parallel to the film plane) and out-of-plane (magnetic field applied perpendicular to the film) configurations using a superconductor quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-5 T) at 300 K.

3. RESULTS AND DISCUSSION

3.1. Structure and Morphology

To analyze the epitaxy and crystal structure of the films, XRD measurements were performed. In **Fig. 1a)** the wide angle θ-*2*θ XRD scans of the films grown on PMN-PT are plotted. θ-*2*θ scans show diffraction peaks in the vicinity of (001) peaks of the substrates. From that it can be concluded that the films have the same *out-of-plane* orientation as the substrate.

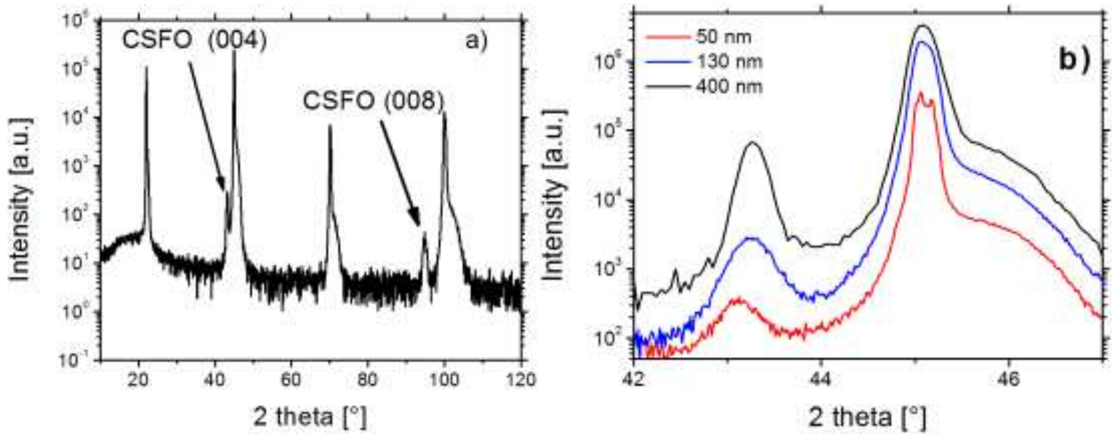

Fig. 1 a) X-ray diffraction patterns (Bragg-Brentano θ-2θ) of the 130 nm films on PMN-PT (001) and **b)** θ-2θ scans around the substrate's (002) peak and CSFO film's (004) peak grown PMNPT

There are no peaks corresponding to other phases or impurities of films on PMN-PT (001) even in the logarithmic scale we have no trace of any impurity peak. The lattice parameters of the films were determined from θ-*2*θ scans around the (004) peak and (044) peak of the CSFO films using the Bragg law. The *out-of-plane* lattice parameters *c* of the films are calculated from the symmetric θ-*2*θ scans around the substrate's (002) peak and CSFO film's (004). The θ-2θ scans for the films with different thickness grown on PMNPT are shown in **Fig. 1b)**. We find that the peak position of the film is shifting slightly to the right with increasing thickness, indicating a decrease of the *c* parameter and a relaxation of the film lattice. The lattice misfit between CSFO and PMN-PT is large (-4.45 %) and provides compressive stress. Scan curves around the asymmetric (044) reflection of the CFO film were used to determine the in-plane lattice parameters. All in-plane and out-of-plane lattice parameters are summarized in **Table 1**.

Table 1 In- and out-of-plane lattice parameters of the films.

Sample	Substrate	$a_{substrate}$	Strain (%)	c $_{film}$	a $_{film}$
		A			
SR58-PMN-PT	PMN-PT	4.022	0.220	8.397	8.402
SR52-PMN-PT	PMN-PT	4.022	0.394	8.364	8.431
SR59-PMN-PT	PMN-PT	4.022	0.367	8.383	8.429

The in-plane epitaxy is confirmed by φ-scans rotating the sample in the (022) and (044) lattice plane of the cubic substrate and film, respectively. **Fig. 2** shows the measurements for the 400 nm films on PMNPT. We find that both, the film and the substrate, exhibit peaks every 90°, which are perfectly at the same position. This confirms the four-fold symmetry of the lattice of the film along this reflection, as it is expected for the cubic structure of the spinel phase. The coincidence with the substrate peaks demonstrates excellent in-plane epitaxy.

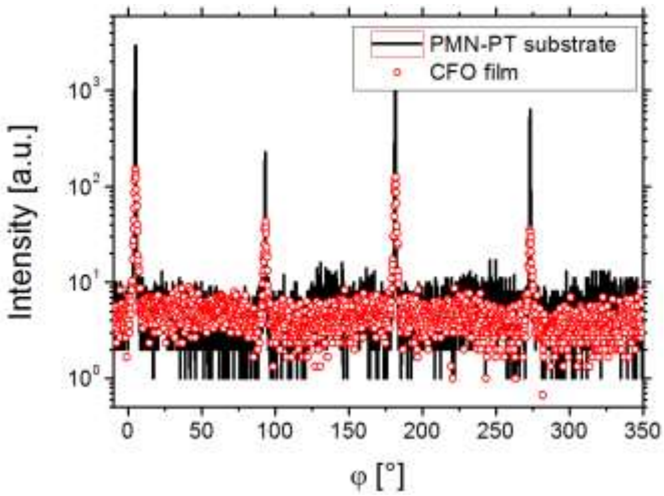

Fig. 2 φ-scans in (022) lattice plane of the cubic PMN-PT substrate and (044) of CSFO 400 nm film

Atomic force microscopy (AFM) was used to investigate the surface of the films. AFM images (**Fig. 3**) reveal a film surface with the typical island-like growth and a reasonable good roughness.

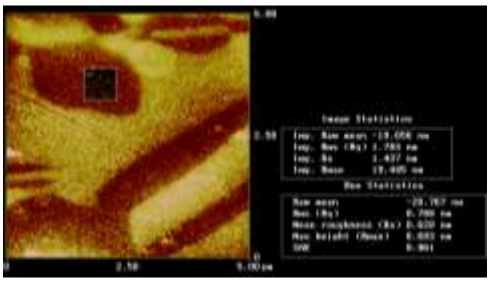

Fig. 3 Surface morphology image of a 50 nm film taken by AFM

3.2. Direct strain measurements

The advantage of direct strain measurements with PMN-PT substrates is the possibility to study the pure effects of controlled strain by using the converse piezoelectric effect, while keeping the extrinsic factors fixed [17]. Here we show that the magnetic anisotropy change is the main result of biaxial strain. The relative change of the remanent magnetic moment is expected to decrease with applying voltage, since the out-of-plane magnetic anisotropy is reduced. A voltage U=350V has been applied to the PMN-PT during SQUID measurement to record the strain-induced change of anisotropy of the films. A biaxial in-plane compression of 0.1% at E = 10 kV/cm has been reported when a voltage of U<350 V is applied along substrate normal [14]. The magneto electric coupling mainly results from the magnetic-mechanical-electric interaction through the stress and/or strain transforming from one subsystem to another. In correlation with the as-grown strain of the films we observe that the easy axes are out of plane for all thicknesses. In **Fig. 4a), b) and c)** we present the changes of the in-plane hysteresis loop of the 50, 130 and 400 nm CSFO film grown on PMN-PT induced by piezoelectric strain.

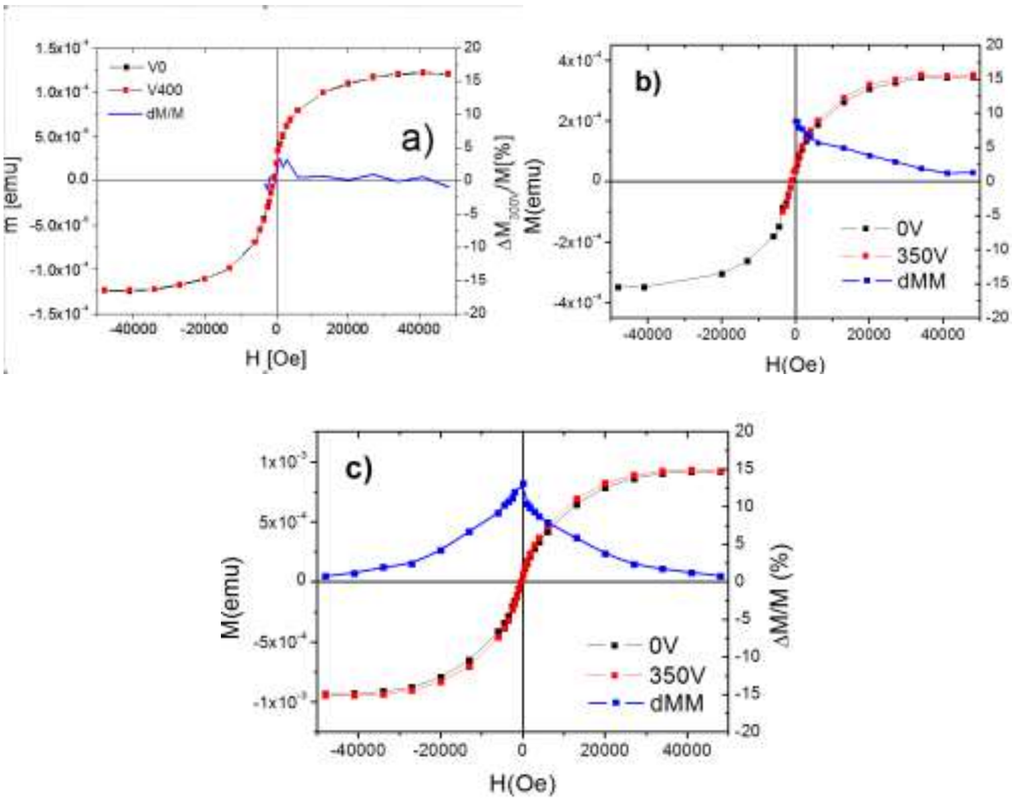

Fig. 4 The changes of the in-plane hysteresis loop of a a) 50 nm b) 130 nm c) 400 nm CSFO film grown on PMN-PT

Cobalt ferrite films presents a relative variation of the residual magnetization of 13.5 % [18] which is approximately 45 % higher than the effect found for CSFO films. One possible explanation is the reduction of the magnetostriction coefficient with the substitution of Sn. It is well known that Co ions play a key role in obtaining a large magnetostriction of $CoFe_2O_4$. However, substitution with Sn leads to a change in the magnetic interactions by reducing the amount of magnetic ions or by varying the degree of inversion in spinel structure. In **Fig. 5** we plot the strain-induced change of the in-plane remanent magnetization (M_r) versus the thickness of the films.

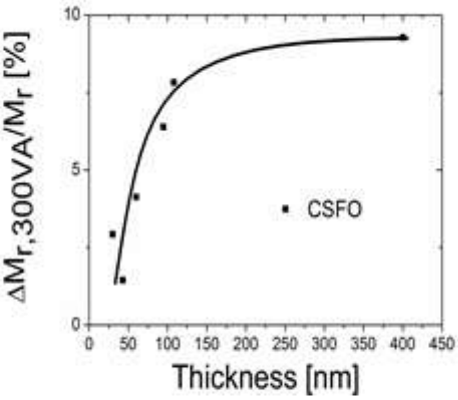

Fig. 5 Strain-induced change of the in-plane remanent magnetization versus the thickness of the films

The relative change of magnetic moment is represented by blue curve from where we can conclude that the biggest change is at 0 applied magnetic fields, respectively on remanent magnetization. The biggest relative change observed for 50 nm thin film is around 3 %. The measurement also presents some scattering because of the small moment. The in-plane hysteresis loop is very slim, with a small coercive field and almost vanishing M_r. The film with the intermediate thickness of 130 nm shows a relative change of 7.8%. The biggest strain effect is recorded for the 400 nm thick film. The E-field-controlled contraction of the substrate of 0.1% for E=10 kV/cm induces a relative change in magnetic moment of 9.3 % when the applied magnetic field is 0. Thus, our measurements reveal a thickness dependence of the strain effect on the magnetic properties of the CSFO films.

CONCLUSION

The work has been devoted to the growth of $Co_{0.9}Sn_{0.1}Fe_2O_4$ as thin epitaxial films using pulsed laser deposition technique. The strain states of the epitaxially grown films are controlled reversibly by strain transfer from piezoelectric $Pb(Mg_{1/3}Nb_{2/3})_{0.72}Ti_{0.28}O_3$ (001) (PMN-PT) substrates. All films are under small tensile strain and have an out-of- plane magnetic easy axis due to large negative magnetostriction. Our reversible strain measurements show that the magnetic anisotropy can be efficiently altered by the application of an electric field to the ferroelectric PMN-PT substrates. The biggest relative change in remanent magnetization we found to be for thickest films of CSFO.

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