Magnetization reversal in NiFe$_2$O$_4$/SrTiO$_3$ nanoheterostructures grown by laser molecular beam epitaxy

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Abstract. NiFe$_2$O$_4$/SrTiO$_3$(001) nanoheterostructures have been fabricated by laser molecular beam epitaxy method. Surface morphology and crystal structure of Ni-ferrite films were analysed by atomic force microscopy (AFM), reflection of high energy electron diffraction (RHEED), X-ray diffraction (XRD). X-ray methods prove the presence of inverse spinel crystal structure of films that was confirmed by measurements of spectral dependence of optical polar Kerr (PMOKE) effect. Study of magnetization reversal for different orientations of magnetic field carried out by vibration sample magnetometry (VSM) and longitudinal magneto-optical Kerr effect (LMOKE) are presented. In-plane magnetization loops exhibit 90° period indicating presence of biaxial magnetic anisotropy. Asymmetry of LMOKE hysteresis loops is related to manifestation of quadratic in magnetization effects in reflection of light.

1. Introduction

Current development of spintronics and magnonics is related in part with the search and study of high quality few nanometer thick magnetic films with high value of magnetization at room temperature and low magnetic losses. For this reason, recently, numerous studies of ferrite films with garnet (R$_3$Fe$_5$O$_{12}$, where R is Ytrrium or rare earth ions), and spinel structure (AFe$_2$O$_4$ where A = Ni, Co, Mn) grown on different substrates have been carried out [1,2].

Nickel ferrite (NiFe$_2$O$_4$, NFO) attracts considerable attention because of higher magnetic moment $M_s$ than that of iron garnets, and relatively low microwave losses [3]. Studies of NFO films grown by laser molecular beam epitaxy (LMBE) method on different substrates reveal high values of magnetization and small width ($\Delta H$) of FMR lines. Possible tuning of NFO film magnetic properties by strain and composition modulation was reported in Ref. [4]. In particular, different orientation of easy axis (out-of-plane and in-plane) was observed in structures grown on MgO and STO substrates. Effect of growth temperature on magnetic properties of NFO/MgO structures and possible increase of magnetization due to redistribution of Ni$^{2+}$ ions to their equilibrium octahedral sites is reported in Ref. [5]. Influence of substrate material, in particular spinel MgAl$_2$O$_4$ (MAO) and perovskite SrTiO$_3$ (STO) substrates, on magnetic properties of NFO films was demonstrated in Ref. [6].
It is well known that static magnetic properties, mechanisms of magnetization switching and parameters related to these mechanisms are very useful for applications and important for characterization of magnetic films quality. In this work, we studied the magnetization reversal process in NFO films grown by LMBE on SrTiO₃(001) substrates. The choice of SrTiO₃ was related with its cubic structure, commercial availability and remarkable properties such as very high value of dielectric constant.

2. Experimental

Epitaxial NFO films (40-220 nm) were grown by ablation of stoichiometric NiFe₂O₄ target in O₂ (P=0.005-0.05 mBar) using irradiation of KrF excimer laser. Commercially available STO(001) substrates were used. The growth temperature was in 500-800°C range. To improve the magnetic properties after the growth, the samples were annealed at 1100°C during three hours in the air. Some of samples were investigated both before and after annealing. In this paper we present results only for the annealed samples.

Surface morphology of the films was analyzed by atomic force microscope (AFM) produced by NT-MDT. Crystal structure of NFO films was studied in situ by reflection high-energy electron diffraction (RHEED) and ex situ by X-ray diffraction.

Magnetization reversal has been studied by vibrating sample magnetometer (VSM) for in-plane and out-of-plane magnetic fields as well as by magneto-optic set-ups utilizing polar (PMOKE) and longitudinal (LMOKE) Kerr effects. LMOKE and PMOKE measurements were carried out using lasers operating at 405 nm and 532 nm wave length and polarization modulation. In PMOKE measurements the orientation of magnetic field H (up to +/- 20 kOe) and direction of incidence light were practically perpendicular to the sample surface. LMOKE measurements were carried out for in-plane magnetic field (up to +/- 4 kOe) scanned with period τ ~ 2 s. Details of experimental setup were described in Ref. [7].

Spectral dependence of PMOKE has been studied in 1-4 eV photon energy range in slowly alternating magnetic field with use of grating monochromator equipped by a halogen source of light. Spectral resolution Δλ/λ, was 1 meV. Modulation of magnetic field was in the range (-10, +10) kOe with the frequency ~ 2 Hz. The angle between polarizer and analyzer was set 45°, the light incidence angle θ ~ 54°. The polarization plane rotation due to PMOKE has been calculated from variations of reflected light intensity. All measurements were carried out at the room temperature.

3. Results and discussion

The spinel crystal structure of NFO layers was confirmed in situ by RHEED (figure 1a) and ex situ by X-ray diffraction. Anomalous X-ray diffraction near K-edges of Ni and Fe indicated that the spinel structure is inverted, which was independently confirmed by the X-ray magnetic circular dichroism measurements [8].

![Figure 1. Typical RHEED (a) and AFM (b) images of NFO film surface](image)
Atomic force microscopy measurements showed flat surface morphology of as–grown samples with the RMS roughness about 0.5 nm at 2×2 micrometers area. The film was formed by small closely packed islands, figure 1b.

Inverse spinel crystal structure of NFO films is indirectly confirmed also by PMOKE spectral dependence shown in figure 2. Spectral dependence of polar Kerr effect (figure 2a) clearly shows S-shaped behavior in polarization plane rotation at E ~ 2.6 eV. Such feature has been also observed previously in both NFO bulk samples and films [9], and was attributed to inter-sublattice charge transfer electronic transition (Fe$^{3+}$)$_2$→[Fe$^{3+}$]$_{2g}$. This transition is allowed when Fe$^{3+}$ ions are distributed between octahedral 16d and tetrahedral 8a positions like in inverse spinel structure. Because in normal spinel structure Fe$^{3+}$ ions occupy only octahedral d - positions such behavior should not exist.

![Figure 2a](image1)
![Figure 2b](image2)

**Figure 2.** Spectral dependence of PMOKE (a) and magnetization curves measured by VSM and PMOKE (b) in grown at 850°C 110 nm thick representative sample.

Figure 2b shows magnetization curves measured in grown at 850°C 110 nm thick structure for out-of-plane magnetic field measured by VSM and PMOKE. Such dependence is typical for all annealed NFO/STO structures. The magnetization M in the films in absence of magnetic field lies in-plane, and the out-of-plane magnetic field H results in reversible magnetization rotation. Magnetization saturation for out-of-plane magnetic field is reached at magnetic field $H_s = 4\pi M_{eff} = 4\pi M_s = H_a$. The value of effective magnetization in this structure $4\pi M_{eff} \approx 3.1$ kG is close to the saturation magnetization $4\pi M_s = 3.47$ kG measured by VSM that indicates relatively small out-of-plane uniaxial anisotropy $H_a \sim (200-300)$ Oe.

Magnetization reversal caused by in-plane magnetic field H in annealed structures clearly shows 90° period indicating the biaxial magnetic anisotropy. Such anisotropy is characterized by two mutually perpendicular easy axis EA$_{1,2}$ and two hard axes HA$_{1,2}$ oriented under angle 45° to EA$_{1,2}$. Figure 3a presents typical angular dependence of coercive field in such structures.
Figure 3. Typical angular dependence of $H_c$ in annealed NFO/STO structures (a). LMOKE magnetization loops in annealed structure for $H || E_{A1}$ (b) and for magnetic field declined from HA on $+/- 5^\circ$ (c).

The magnitude of coercive field in annealed structures $H_c \leq 100$ Oe is much smaller than that $H_c \sim (300-400)$ Oe in as grown ones. Orientation of magnetic field parallel to $HA_{1,2}$ is followed by spikes in angular $H_c$ dependence.

The shape of hysteresis loops is angular dependent and exhibits $90^\circ$ period. Hysteresis loops measured for magnetic field parallel to easy axes ($E_{A1}$ or $E_{A2}$) have rectangular shape, figure 3b. For other orientations of in-plane magnetic field the LMOKE hysteresis loops (polarization rotation and ellipticity) reveal strong asymmetry (figure 3c) indicating the contribution of quadratic in magnetization optical effects proportional to $M_xM_y$ [10-13]. Second order magneto-optical effects in films of tetragonal or cubic symmetry in reflection of light may be proportional to combination of magnetization components $\sim M_xM_y$ or $\sim (M_x^2 - M_y^2)$, where axes X,Y are oriented in-plane parallel (X) and orthogonal (Y) to applied field [12, 11]. These effects does not manifest itself for $H || E_{A1,2}$ because the magnetization reversal goes only through domain wall nucleation and motion without magnetization rotation. In vicinity of $HA_{1,2}$ the contribution of $(M_x^2 - M_y^2)$ term is negligible [12] and contribution of second order effects is related mainly to $M_xM_y$-term. Magnetic field dependence of these effects is symmetrical, i.e. $L(H) = L(-H)$, in contrast to linear in magnetization effects (i.e. LMOKE) in which $L_{as}(H) = -L_{as}(-H)$.

It is noteworthy that the second order effects may be of the same order of magnitude as linear ones and can very strongly change the shape of hysteresis loops. Figure 4 presents experimental hysteresis loop in NFO/STO structure measured in LMOKE geometry at 405 nm in vicinity of HA and the symmetrical part of loop obtained by mathematical decomposition of the loop on symmetric and anti-symmetric part. Figure 4 shows that the decrease of the field from their maximal values to zero is followed by magnetization rotation from HA to the nearest $E_{A1}$ and increase of $M_y$ component. At $H = H_c$ the magnetization jumps to another $E_{A2}$, stay there in magnetic field interval and then rotates to the magnetic field direction. Using $M_x$ and $M_y$ extracted from the decomposition one can calculate trajectory of magnetization, shown in figure 4c. Two step magnetization reversal for magnetic field
close to HA is confirmed also by VSM measurements in the case of in-plane magnetic field oriented in vicinity of HA, figure 4 d. Note that analogous trajectories were found in the case of Fe/ MgO(001) structures [12, 13].

**Figure 4.** LMOKE hysteresis loop at λ = 405 nm in NFO/SNO structure in vicinity of HA (a). Symmetrical part of hysteresis loop obtained by mathematic decomposition (b). Trajectory of magnetization for orientations of magnetic field along EA and in vicinity of HA (c). Magnetic hysteresis loop measured by VSM for in-plane magnetic field oriented under angle 20° to HA (d).

4. **Conclusions**

In conclusion, nanosized NFO films have been fabricated on STO(001) substrates by LMBE method. Ni-ferrite films grown epitaxially on STO have inverse spinel crystal structure. In-plane magnetization orientation in obtained structures is caused mainly by the form factor. Induced magnetic anisotropy is much smaller indicating small deformations of film by the substrate. In-plane magnetization curves measured by LMOKE clearly show biaxial magnetic anisotropy which manifest itself in angular dependence of coercive field and shape of loops. Hysteresis loops measured in LMOKE geometry reveal strong contribution of second order magneto-optical effects which result in considerable symmetric in magnetic field part. Analysis of quadratic in magnetization effects show two-step magnetization reversal in vicinity of HA confirmed also by VSM measurements of magnetization.
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