Magnetite Thin Films Grown by Pulsed Electron Deposition for Spintronic Applications

Belenchuk A., Shapoval O.
IIEN, Academy of Sciences of Moldova,
Chișinău, Republic of Moldova

Alek Dediu V.
ISMN, Consiglio Nazionale delle Ricerche,
Bologna, Italy

***Abstract*—We report on the growth and properties of magnetite, Fe_3O_4, thin films on spinel substrates. Raman studies confirmed growth of single-phase magnetite, but X-ray diffraction analysis reveals a non-uniform structure of the films with a strained pseudomorphic layer. Transport properties of the films are well satisfied to the magnetite ones, but magnetization is significantly reduced than it can be expected for a high quality magnetite. We explain these results within the concept of dead magnetic layer situated close to the film/substrate interface resulting in the coexistence of different magnetic phases within a uniform crystal phase of magnetite.**

***Keywords*—Magnetite, thin films, pulsed electron deposition, structure, magnetic and transport properties**

I. Introduction

Organic spintronics, by combining inorganic ferromagnetic electrodes with organic layers, is now attracted much attention due to several orders higher spin relaxation time in organic semiconductors as compared with inorganic ones [1]. However, achieving a large magnetoresistance effect at room temperature in organic spin valves is still challenging because of the low Curie temperature of the $La_{0.7}Sr_{0.3}MnO_3$ manganite, which is usually used as a spin injection electrode [2]. Therefore, a search of an alternative ferromagnetic material for more efficient spin injection at room temperatures is highly demanded problem.

The oldest known magnetic material, magnetite, is ferrimagnetic half-metal with predicted 100% spin polarization at the Fermi energy and the highest known Curie temperature of 858 K [3]. Recently, a relatively large room temperature magnetoresistance of 4−6 % have been achieved by applying of the magnetite thin film as electrode for spin injection [4]. But obtaining of the required long-range ordering in complex spinel structure of magnetite is exceptionally difficult epitaxial task, so up to now the achievement of bulk-like degree of spin polarization at room temperature has not been demonstrated [5]. While a lot of epitaxial techniques have been applied, the pulsed laser deposition (PLD) approach to the growth of complex oxide films is the most common due its unique ability to produce a film material with the same stoichiometry as a target source. However, PLD technique requires using an expensive excimer laser and optics. Therefore, introduction of a new and inexpensive method of electron beam deposition (PED) may by more convenient. In addition to the economic reasons, using of electron beam for ablation has advantage in the smaller absorption depth of electrons as compared to photons that allows to ablate transparent materials [6]. The ability for PED to grow magnetite using reducing of Fe_2O_3 in Ar/H_2 atmosphere has been already demonstrated for a specific case of deposition on the surface of organics [7].

Here we report results on an epitaxial growth of magnetite by PED from a stoichiometric Fe_3O_4 target in a pure Ar atmosphere on spinel ($MgAl_2O_4$) substrate and present their structural, magnetic and transport properties.

II. Experimental Results and Discussion

Custom build PED system, where the high-energy electron beam is generated by means of a channel spark discharge, was used for magnetite growth. The deposition was performed at the Ar pressure $1{-}2{\times}10^{-2}$ mbar. Substrates of (100)−oriented $MgAl_2O_4$ single crystals were kept at temperatures 250−450°C during the growth. Rates of deposition from 0.01 to 0.05 Å/pulse were obtained at 3–6 Hz pulse repetitions and acceleration voltages of 15–18 kV.

The morphology of Fe_3O_4 thin films was characterized by atomic force microscopy (AFM). Figure 1 shows a typical example of magnetite surface morphology. Except for some outgrowths, which are occasionally presented on the surface due to some particles ablation from the target, the magnetite films has flat surface with a root mean square (RMS) of roughness equal to 0.4 nm for the given image.

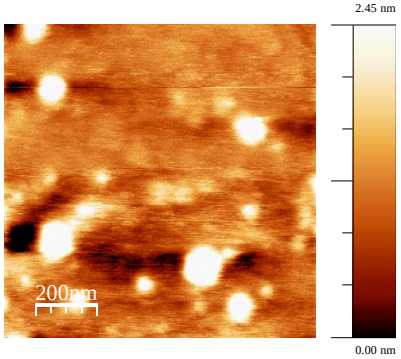

Fig. 1.AFM observation of surface of 11 nm thick Fe_3O_4 grown at 350°C.

Thickness and smoothness of magnetite films were studied by a small-angle x-ray scattering (SAXS) in a Brucker D8 diffractometer. Fig. 2 shows a typical example of SAXS pattern from magnetite thin film. Distinct small-period oscillations, which are originated from a total film thickness, were observed up to 4 degrees, confirming both the film surface and substrate/film interface smoothness's.

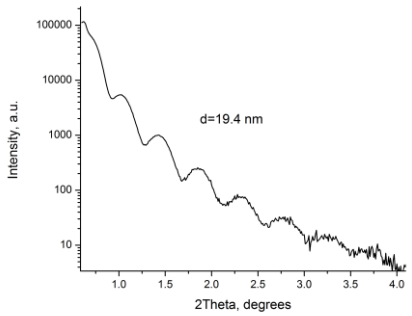

Fig. 2. SAXS pattern from 120 nm thick magnetite film grown at 450°C.

Phase purity of the films was measured by micro-Raman spectroscopy that is very sensitive to different phases of iron oxides [8]. Raman spectra were studied at room temperature with the Renishaw 1000 micro-Raman spectrometer. At all used growth conditions the Raman measurements confirmed obtaining of single phase composition of magnetite and its homogeneity over the whole film surface. Raman spectrum taken from a relatively thick film is shown on Fig. 3.

X-ray diffraction (XRD) analysis was also performed in a Brucker D8 diffractometer. A typical XRD spectrum around the $MgAl_2O_4$ (100) Bragg peak of substrate is shown on Fig. 4. For all obtained films, besides the Fe_3O_4 (400) peak, we always observed the presence of an additional peak that was situated near Fe_3O_4 (400) peak at smaller angles. The intensity of this additional peak increased relative Fe_3O_4 (400) as far as the total thickness of film decreased. This dependence can be explained taking into consideration the possibility of a pseudomorphic growth of magnetite on the isostructural spinel substrate that has a relatively low lattice mismatch with magnetite. Since the lattice parameter of $MgAl_2O_4$ is equal to 0.8083 nm and smaller than lattice parameter of Fe_3O_4, which is 0.8399 nm, we can conclude that strained pseudomorphic layer near the substrate should be compressed in the substrate plane. Therefore, in a normal to substrate direction the lattice should be respectively producing the additional XRD peak at a smaller angle.

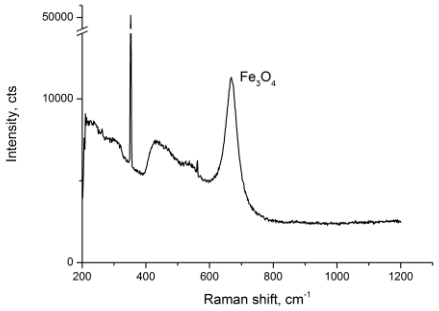

Fig. 3. Raman spectrum of 0.4 μm thick Fe_3O_4 grown at 450°C.

Magnetic measurements were carried out by using a commercial superconducting quantum interference device (SQUID) magnetometer, from Quantum Design, at temperatures of 5−400 K with magnetic field aligned parallel to the film surface.

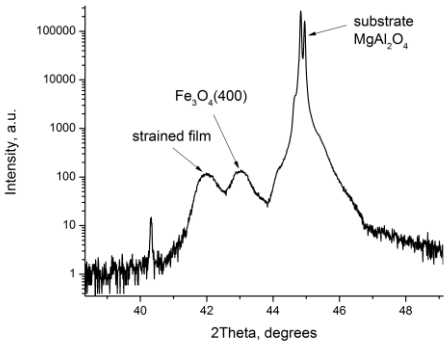

Fig. 4. X-ray diffraction for 18 nm thick Fe_3O_4 film grown at 450°C.

Figure 5 shows the room temperature magnetic moment loop that confirms ferromagnetism of thin film material. However, the obtained saturation magnetization, ~ 230 emu/cm^3, is about twice smaller than it can be expected for a singe crystal magnetite, which possesses ~ 480 emu/cm^3 for the bulk single crystals. Temperature dependence of magnetization was rather weak reaching a value of ~ 300 emu/cm^3 at 5 K. In spite of the reduced magnetization, the obtained thin film material was very soft with coercive fields of ~ 10−15 Oe for thicknesses of 10−20 nm. The magnetic softness reflects a high microstructural perfection (absence of pinning centers) for the magnetite grown on isostructural spinel substrate.

The same magnetic properties, the reduced magnetization and small coercivity, were obtained with measurement of the magnetooptical Kerr effect (MOKE) at room temperature. MOKE signal was collected in the longitudinal and transversal configurations using He–Ne laser line (P=5 mW). Fig. 6 shows the hysteresis loop with coercive field of ~ 10 Oe at 300K for MOKE signal in a longitudinal configuration. Values of magnetization that were measured by MOKE coincided with those obtained by SQUID.

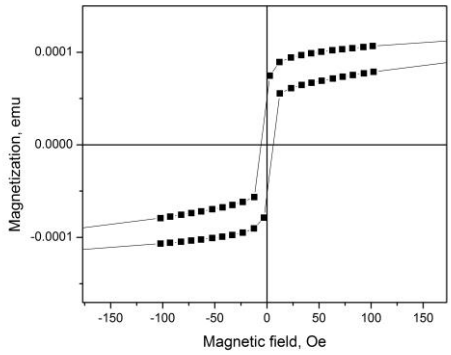

Fig. 5. Hysteresis curve at 300K for 11 nm thick grown at 350°C.

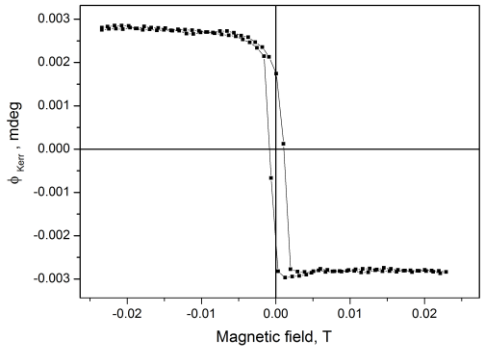

Fig. 6. MOKE measurement on a 18 nm thick Fe_3O_4.

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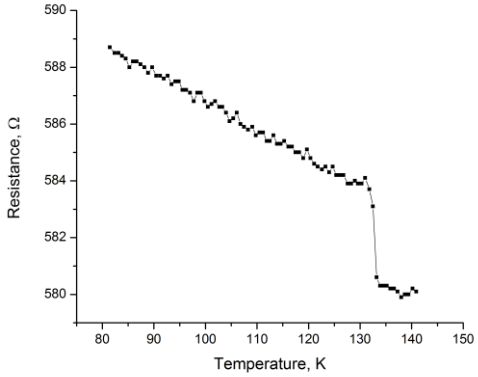

Fig. 7. Temperature-dependent resistance of a 11 nm thick magnetite film.

Four-probe resistance measurements by using silver paste contacts were performed in a N_2 cryostat. The temperature dependence of resistance for an 11 nm thick magnetite films is shown on Fig. 7. A jump like behavior in the resistance around 130–135 K temperature range corresponds to the Verwey transition in magnetite, confirming a relatively high degree of Fe-ion ordering in the grown magnetite. Room temperature resistivity is equal to ~ 3×10^{-3} Ωcm and this value is well correspond to the values inherent in a bulk single crystalline magnetite.

III. Conclusions

The films grown on spinel substrate by PED from Fe_3O_4 target in pure Ar atmosphere are consisted from single phase of magnetite as it was proved by the Raman measurement. Both a very low resistivity and a small, but still clearly visible Verwey transition, confirmed also synthesis of a pure magnetite phase. However, XRD analysis revealed a non-uniform crystalline structure of the grown films with a highly strained layer. This layer, being probably a highly strained pseudomorphic epitaxial layer, is situated at the film/surface interface and formed due to a significant lattice mismatch with substrate at the beginning of growth. The magnetic measurements with SQUID and MOKE revealed a ferromagnetic behavior with a very low coercivity, but with about twice reduced saturated magnetization than it should be for a homogeneous magnetite We suggest that the decreasing of magnetization is attributed to the formation of a dead magnetic layer, which is produced within a highly strained layer near the substrate due to mismatch stress at the film/substrate interface. It is well known that the dead magnetic or electric layers are often considered as a possible reason for anomalous properties of complex oxides and, for example, for the epitaxial magnetite films [9].

In spite of a reduced value of magnetization, the obtained magnetite films, possessing a very low coercivity at room temperature, can be served as an appropriate material for fabrication of magnetic field sensors.

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