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Polycrystalline magnetite (Fe_3O_4) thin films from FeO_x/Fe bilayers grown by pulsed laser depositions

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ABSTRACT

The effect of heat treatment on the structural and magnetic properties of bilayered FeO_x/Fe thin films grown by pulsed laser deposition on pre-oxidized amorphous SiO_2/Si substrates has been studied. Post-deposition vacuum thermal annealing leads to remarkable changes in the structural and magnetic properties of the FeO_x layer, which has been investigated by the combination of scanning electron and atomic force microscopy, Raman scattering spectroscopy and conversion electron Mössbauer spectroscopy. FeO_x layer deposited at room temperature on top of the polycrystalline Fe underlayer is amorphous with the smooth surface (root mean square roughness ~0.5 nm). Vacuum thermal annealing of the FeO_x/Fe stack at T = 500 °C leads to the formation of a polycrystalline Fe_3O_4/Fe thin film structure with the magnetite nucleation centers of an average size of 100 nm. The formation of the exact magnetite phase depends on the annealing conditions as shown by in-situ Raman and Mössbauer spectroscopy investigations.

1. Introduction

Magnetite (Fe_3O_4), which is one of the most investigated magnetic oxides, attracts significant interest due to the prediction of its half-metallic nature, with the dominating minority spin polarization of P = −100% at the Fermi level at T = 0 K [1]. This prediction is based on the band structure calculations, which have been followed by the experimental evidence for P = −80% in Fe_3O_4 thin films [2]. Therefore, thin Fe_3O_4 films are attractive for potential applications in spintronic devices, such as "ideal" electrodes in magnetic tunnel junctions (MTJs) [3–5]. Magnetite also exhibits remnant polarization at low temperatures and being ferrimagnetic at the same time may be considered as a multiferroic material [6,7]. Magnetite also meets important prerequisites for microelectronic applications: its Curie temperature and coercive field are relatively high (T_C ~ 585 °C and H_C ~ 0.01–0.04 T, respectively) [8]. However, the shape of hysteresis loops experimentally observed in up to 1 μm thick Fe_3O_4 films is far from an ideal rectangle, displaying smoothed corners with the remnant to saturation magnetization (MS) ratio < 50% [9]. Also, the values of MS for such films achieve only about 300 kA/m. Epitaxial thin Fe_3O_4 films grown on different substrates, such as MgO (100) [10,11], MgO (110) [12,13], a-Al_2O_3 (001) [14,15], $MgAl_2O_4$ [14,16], and $SrTiO_3$ [14], exhibit anomalous magnetic behavior: in most samples it is impossible to reach MS even in magnetic fields up to 1 T [10,12,14]. Such behavior can be explained in terms of structural anti-phase boundaries, intrinsically existing in thin films of magnetite [9,12,14,17]. The control of the magnetic properties of Fe_3O_4 thin films is a prerequisite to developing the Fe_3O_4-based functional spintronic devices such as MTJs.

In order to improve the magnetic properties of Fe_3O_4, the use of the ferromagnetic buffer layers, particularly, Fe and Cr, has been proposed [11,12]. For instance, the use of thin (~2 nm) buffer Fe (001) or Cr (001) underlayers on MgO (001) substrate revealed dramatic changes of the magnetic properties, particularly, the density of antiphase boundaries, in *heteroepitaxial* Fe_3O_4 (001) (~10 nm) films compared to a single Fe_3O_4 (001) layer [9]. MS of the structures with an ultrathin buffer layer is found to be several times higher compared to a single magnetite layer (up to 800 kA/m).

In our previous work [21], we reported on the improvement of the magnetic properties of Fe_3O_4 grown on the metallic underlayer for *polycrystalline* films. The films were produced by the pulsed laser deposition (PLD) technique – an established method to grow thin films of oxide materials, including stoichiometric Fe_3O_4 [19–21]. Here we report on the evolution of the structure of our *polycrystalline* Fe_3O_4/Fe bilayers upon post-deposition vacuum annealing and discuss the reasons of the improvement of their magnetic properties.

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2. Experimental details

Bilayer FeO_x (105 nm)/^{54}Fe (25 nm) thin films were produced in a PLD setup with a base pressure of 10^{-6} Pa at room temperature (RT) using YAG:Nd laser (λ = 1064 nm, τ = 15 ns, E = 0.05–0.15 J). The laser was focused at ~1 mm spot, and the distance between the substrate and the target was 4 cm. The ablation was sequentially performed from ^{54}Fe (98% enriched, supplied by Sigma-Aldrich) target and the target pressed from Fe_3O_4 powder (95% purity, supplied by Sigma-Aldrich). Si (100) wafers with thermally grown 100-nm oxide layer (supplied by ZAO "Telecom-STV", Zelenograd, Russia) were used as a substrate. As-grown samples were divided into several pieces and annealed in vacuum at temperatures in the range of T = 200–500 °C.

Raman scattering analysis was performed using Horiba T64000 Raman spectrometer with Ar^+ excitation laser operating at the wavelength of 514.5 nm in two different geometries when the polarizations of the incident and scattered light are perpendicular (XY) or parallel (YY) to each other.

Surface morphology was investigated using atomic-force microscope (AFM) SmartSPM Aist-NT in the tapping mode and scanning electron microscope (SEM) Carl ZEISS Crossbeam 540 (system vacuum: 6.8×10^{-7} mbar, accelerating voltage: 3 kV, probe current: 103 pA). Surface roughness was defined as the standard deviation of the height across the area of 1 μm × 1 μm.

^{57}Fe conversion electron Mössbauer spectroscopy (CEMS) has been carried out at RT by using ^{57}Co-source that was moved by a standard constant acceleration drive. The samples were incorporated as an electrode in a parallel plate avalanche counter filled with acetone counting gas, and operating voltage was around 700 V. CEMS has been performed on two separate samples: as deposited and 500 °C vacuum annealed Fe_3O_4/^{54}Fe stacks. The ^{54}Fe character (98%) of the Fe buffer layer allows performing CEMS on the topmost Fe_3O_4 film by exploiting its natural 2.2% ^{57}Fe isotopic abundance. Isomer shifts are given relative to α-Fe at RT.

3. Results and discussion

The magnetic properties of our Fe_3O_4 thin films with Fe buffer layer produced by PLD were published earlier (including M-H hysteresis loops, see Fig. 1, [18]) and are briefly summarized in Table 1: vacuum annealing of the initial films at 500 °C raises the coercive field and saturation magnetization by factors of ~11 and ~1.5 respectively, that makes our polycrystalline films comparable to epitaxial structures reported by the other groups (Fe_3O_4 (100) (20 nm)/Fe (100) (8 nm)//MgO (100), [22]). After the annealing, the shape of the hysteresis loop of our samples becomes rectangular and the coercive force increases above 0.01 T, that makes it possible to meet the requirements for the applications of the polycrystalline Fe_3O_4 films as an electrode in MTJs.

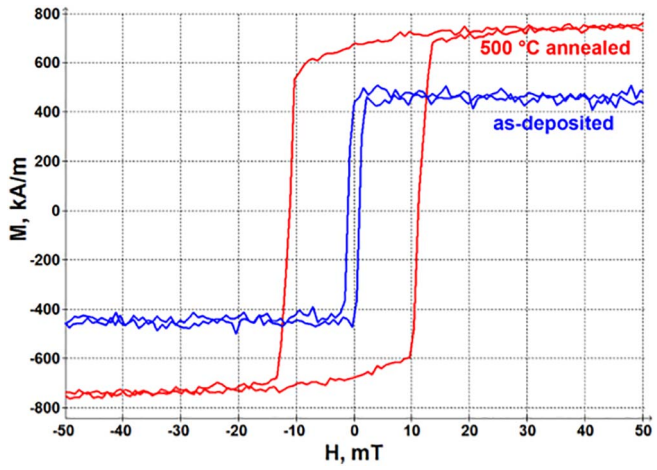

Fig. 1. Hysteresis loops of the Fe/Fe_3O_4 two-layer structures for as-grown and 500 °C vacuum annealed samples, [18].

Table 1
Magnetic properties of Fe_3O_4 layers for different structures.

Structure	H_C, mT	M_S, kA/m
Fe_3O_4 (105 nm)/Fe (25 nm) //SiO_2/Si, 500 °C [present study]	14	700
Fe_3O_4 (20 nm)/Fe (10 nm) //SiO_2/Si, 20 °C [18]	1	490
Fe_3O_4 (20 nm)/Fe (10 nm) //SiO_2/Si, 500 °C [18]	11	760
Fe_3O_4 (20 nm)/Fe(8 nm) //MgO [22]	8.5	870

In the present study, we produced thicker films to facilitate the structural investigations of the samples. After the annealing, Fe_3O_4 (105 nm)/Fe (25 nm)//SiO_2/Si structure demonstrated approximately the same magnetic properties as our structures published earlier ((Fe_3O_4 (10 nm)/Fe (20 nm)//SiO_2/Si) [18], see Table 1).

In order to understand the origin of the change of the magnetic properties, we conducted the Raman scattering measurements for both as-grown and vacuum annealed (T = 500 °C) FeO_x (105 nm)/Fe (25 nm)//SiO_2/Si samples, and the results are shown in Fig. 2. As-grown samples exhibit one low-intensity peak around 668 cm^{-1} for YY geometry (Fig. 2a) and two small features around 539 and 314 cm^{-1} for XY geometry (Fig. 2b). These peaks can be attributed to A_{1g}, T^2_{g2} and T^3_{g2} magnetite vibrational modes, respectively [23]. The low intensity of the Raman signal evidences that the FeO_x film is almost amorphous. In contrast, FeO_x/Fe bilayer annealed at T = 500 °C in vacuum, exhibits much stronger signal suggesting the film crystallization into Fe_3O_4 phase. YY geometry suppresses T_{2g} Raman lines, and indeed the most prominent feature of the spectrum in Fig. 2a is located around

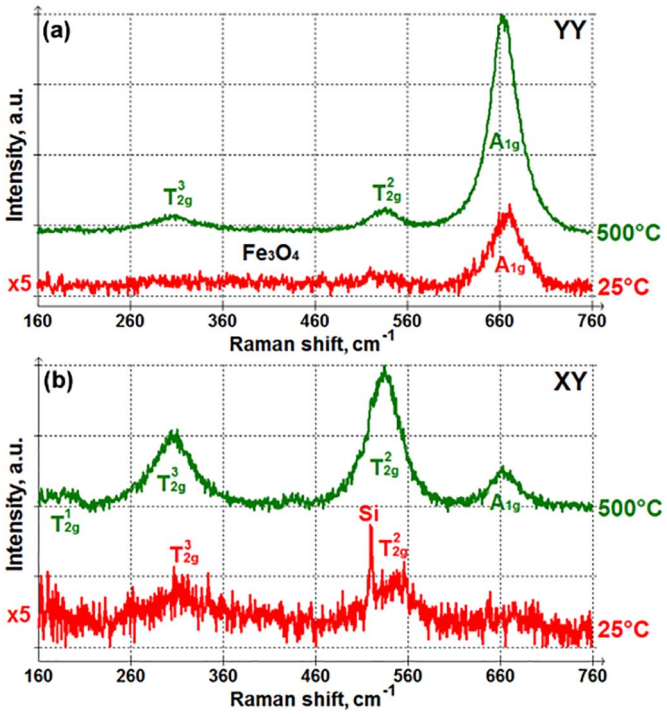

Fig. 2. Raman spectra for the FeO_x/Fe bilayer: a) in YY and b) in XY geometries. Bottom (red) curves correspond to the as-grown samples and top (green) curves correspond to the samples annealed at T = 500 °C at vacuum. The intensities of the spectra for as-grown samples are multiplied by the factor of 5. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)