High surface stability of magnetite on bi-layer Fe$_3$O$_4$/Fe/MgO(001) films under 1 MeV Kr$^+$ ion irradiation

N-T H Kim-Ngan$^1$, M Krupska$^1$, A G Balogh$^2$, P Malinsky$^3$ and A Mackova$^{1,4}$

$^1$ Nanostructure Laboratory, Institute of Physics, Pedagogical University, Podchorazych 2, 30 084 Krakow, Poland
$^2$ Institute of Materials Science, Technische Universität Darmstadt, Petersenstr. 23, 64287 Darmstadt, Germany
$^3$ Nuclear Physics Institute, The Academy of Sciences of the Czech Republic, v.v.i., 25 068 Rez, Czechia
$^4$ Faculty of Science, Department of Physics, J.E. Purkinje University, Ceske Mladeze 8, 400 96 Usti nad Labem, Czechia

E-mail: tarnawsk@up.krakow.pl

Received 7 June 2017
Accepted for publication 18 July 2017
Published 29 August 2017

Abstract

We investigate the stability of the bi-layer Fe$_3$O$_4$/Fe(001) films grown epitaxially on MgO(001) substrates with the layer thickness in the range of 25–100 nm upon 1 MeV Kr$^+$ ion irradiation. The layer structure and layer composition of the films before and after ion irradiation were studied by XRR, RBS and RBS-C techniques. The interdiffusion and intermixing was analyzed. No visible change in the RBS spectra was observed upon irradiation with ion fluence below 10$^{15}$ Kr cm$^{-2}$. The bi-layer structure and the stoichiometric Fe$_3$O$_4$ layer on the surface were well preserved after Kr$^+$ ion irradiation at low damage levels, although the strong intermixing implied a large interfacial (Fe$_x$O$_y$) and (Fe, Mg)O$_y$ layer respective at Fe$_3$O$_4$–Fe and Fe–MgO interface. The high ion fluence of 3.8 $\times$ 10$^{16}$ Kr cm$^{-2}$ has induced a complete oxidization of the buffer Fe layer. Under such Kr fluence, the stoichiometry of the Fe$_3$O$_4$ surface layer was still preserved indicating its high stability. The entire film contains Fe$_{x}$O$_{y}$-type composition at ion fluence large than 5.0 $\times$ 10$^{16}$ Kr cm$^{-2}$.

Keywords: 2.00 nanoscience, 4.10 thin film, 4.14 surface and interface
Classification numbers: 2.00, 4.10, 4.14

1. Introduction

Iron oxides, magnetite (Fe$_3$O$_4$), maghemite ($\gamma$-Fe$_2$O$_3$), hematite ($\alpha$-Fe$_2$O$_3$) and wüstite (FeO$_x$), form naturally of Fe-containing rocks. They play an important role where they exist everywhere (in rocks (both on lands as well as in oceans), soils and dust in the atmosphere) and have integrated in many biological systems including the human body tissues. Magnetite (Fe$_3$O$_4$)—the oldest known magnetic material has been studied since the early days of science. Since the 1960s magnetite has been investigated extensively due to its high potential for technological applications in many important fields, e.g. high-density recording media and catalysis [1]. Magnetite crystallizes into a cubic inverse spinel structure and is a ferrimagnet below 858 K ($T_N$) with a net magnetic moment of 4.1 $\mu_B$ per formula unit. The coexistence of Fe$^{2+}$ and Fe$^{3+}$ ions in the octahedral sublattice leads directly to many interesting properties, e.g. the Verwey transition around 123 K [2–4]. In recent years, magnetite has attracted again much attention, since it is referred as a half-metallic material having a predicted full spin polarization at the Fermi level and thus considered as a promising candidate for spintronic devices at room temperature utilizing the spin polarised current [5, 6]. Many attempts have been focused on determining...
the spin polarisation of magnetite [7, 8], on using magnetite as electrode in spin valve [9], tunnel magneto-resistance [10–12] and magnetic tunnel junctions [13, 14]. Besides, magnetite has recently exhibited its high potential for biomedical applications, such as Fe3O4-based nanoparticles used as contrast agent for magnetic resonance imaging scanner/diagnosis [15, 16] and as drug delivers/carriers for e.g. anticancer treatments [16–18].

In the last few decades, an increasing interest is focused on the iron oxide surfaces, since they play a major role in e.g. corrosion, catalysis, spintronics and biomedicine [19–21]. In particular a large attention is paid to magnetite films due to their potential application as spin dependent transport devices. Especially, up to 72% mobile electrons were found to be polarized in Fe3O4(001)/MgO(001) films [22]. Besides, using thin films opens an exciting road for future research of surface engineering through absorption, which may permit tailoring of the interfacial spin polarization in magnetite-based spintronic devices [23]. The best understood iron oxide surface at present is probably Fe3O4(001) surface; its structure is known and the major properties are well characterised [24]. The best technique to grow Fe3O4(001) thin films is the reactive molecular beam epitaxial (MBE) deposition utilizing MgO(001) substrate [25]. For a review of surface termination and reconstruction of Fe3O4 surfaces, see references [7, 24–28].

The physical and structural properties of interfaces play a crucial role in obtaining well-oriented thin films. Not only the surface but also the interface can be performance-limiting the practical applications of magnetite. Besides, while a large effort is focusing on the magnetite film surfaces, their interfaces have been less studied. It is thus important to investigate the interfaces and their correlation to the entire-film properties. Moreover, regarding the possible technical applications, it is worth obtaining the knowledge of the stability of the magnetite films in the external conditions, such as high temperature (annealing) and ion irradiations. In fact, there is a lack of the knowledge of interdiffusion and intermixing effects in magnetite films. To the best of our knowledge, there is no report on such a research for Fe3O4 thin films, except of our publications [29–31]. There existed some reports devoted to using the swift heavy ions to modify the magnetic and transport properties of magnetite films [32, 33].

The goal of the present work is to use MeV ion beams to study and modify the structure, composition and properties of magnetite films especially at the interfaces. We are interested in finding the ion fluence upon which the film structure and the Fe3O4 surface layer can be well preserved under ion irradiations. We have exploited Rutherford backscattering (RBS) and RBS-channeling (RBS-C) methods, since they allow the detection of elements in the sub-monolayer range with an electronic energy-loss spectroscopy (EELS) in a multi-chamber UHV system have been reported earlier [26, 27, 34]. We also performed similar experiments on the Fe3O4(001) films prepared in a standard reactive deposition directly on MgO substrates with similar film thickness, e.g. (25 nm)Fe3O4/MgO(001) and (50 nm)Fe3O4/MgO(001) denoted as Fe3O4(25 nm) and Fe3O4(50 nm). By analyzing and comparing the results obtained for films with either a similar layer structure but with different layer thicknesses or with a similar layer thickness but with a different layer structure, we expect to gain a deep understanding of the atomic transport process. These single-layer magnetite films possess a high crystallinity. However, Mg out-diffusion from MgO substrate into the Fe3O4 film implies that entire film or a part of the film has a spinel composition. Indeed, Mg was found to segregate to the surface for the thin film with a thickness <25 nm.

The chemical composition and layer structure of the films in the as-grown state have been determined by a combined Rutherford back-scattering (RBS) and x-ray reflectometry (XRR) analysis. The RBS spectra by using 2 MeV He+ ions at a backscattering angle of 171° were collected and evaluated at different tilt angles φ in the range of 0–45° [28]. SIMNRA simulation program was used for RBS data analysis, taking into account the electronic stopping power data by Ziegler and Biersack, Chu Yang’s theory for electronic energy-loss straggling and Andersen’s screening function to Rutherford cross-section [35]. XRR was performed by using a Seifert two-circle diffractometer (using a rotating anode with 40 kV and 120 mA, and a LiF monochromator and a slit system for separating the Cu-Kα1 line) with the Seifert reflectivity
Table 1. Selected results showing the effect of 1 MeV Kr\(^+\) ion irradiation on bi-layer Fe\(_3\)O\(_4\)/Fe/MgO(001) films (denoted by the nominal layer-thickness) \(d_1\) and \(d_2\) are respectively the estimated layer thickness of the surface Fe\(_3\)O\(_4\) layer and the Fe buffer layer, \(d_{2s}\) is the mixed Fe\(_3\)O\(_4\) layer at the Fe\(_3\)O\(_4\)/Fe interface, \(d_{1s}\) and \(d_{2s}\) are respectively the (commonly-denoted) interfacial (Fe, Mg)O layer between the film and the MgO substrate (see text). The relative decrease of the layer thickness is indicated by the ratio between the layer thickness before (in the as-grown state) and after irradiation \((d_k)\): \(R(\text{Fe}_3\text{O}_4) = d_{1s}/d_1, R(\text{Fe}) = d_{2s}/d_2\), respectively for the Fe\(_3\)O\(_4\) and Fe layer. The results for single-layer Fe\(_3\)O\(_4\)/MgO(001) film are included for a comparison.

| Film (nominal thickness) | \(\phi \times 10^{15}\) (ions cm\(^{-2}\)) | Fe\(_3\)O\(_4\) \(d_1\) (nm) | Fe\(_3\)O\(_4\) \(d_{1s}\) (nm) | Fe \(d_2\) (nm) | (Fe, Mg)O \(d_{2s}\) (nm) | \(R(\text{Fe}_3\text{O}_4)\) \((d_{1s}/d_1)\) (%) | \(R(\text{Fe})\) \((d_{2s}/d_2)\) (%) |
|--------------------------|--------------------------------------|---------------------|---------------------|-----------------|-----------------|-----------------|-----------------|
| Fe\(_3\)O\(_4\) (50 nm)  | As-grown 8.4 (Kr3) 50 0 0 3          |                    |                    |                 |                 |                 |                 |
| Fe\(_3\)O\(_4\)/Fe(25-25 nm) | As-grown 8.4 (Kr3) 28 0 22 5       |                    |                    |                 |                 |                 |                 |
| Fe\(_3\)O\(_4\)/Fe(50-50 nm) | As-grown 16 (Kr2) 59 9 16 30 86 73 |                    |                    |                 |                 |                 |                 |
| Fe\(_3\)O\(_4\)/Fe(100-50 nm) | As-grown 38 (Kr4) 112 47 36 5 63 47 |                    |                    |                 |                 |                 |                 |

The ion beam mixing experiments were carried out using a 1 MeV Kr\(^+\) beam with ion fluence \(\phi\) in the range of \(1.6 \times 10^{15} \text{–} 3.8 \times 10^{16}\) Kr cm\(^{-2}\) (some \(\phi\)-values are listed in table 1). The sample temperature was kept at \(-50^\circ\text{C}\) during irradiations.

The results of XRR and RBS indicate that the initial composition and thickness of the films remain unchanged after irradiation with \(\phi < 10^{15}\) Kr cm\(^{-2}\). Using Kr\(^+\) ions, for obtaining a similar intermixing level, the irradiate time would be much shorter than Ar\(^+\) ions and thus we could avoid the contamination to the films (since the pressure of the standard irradiated chamber is maintained at only around \(10^{-6}\) mbar).

The RBS, RBS-C and irradiation experiments were performed at the Institute of Nuclear Physics of the Johann von Goethe University in Frankfurt/Main (IKF-Frankfurt). We also used the second RBS equipment\(^5\) with 1.7 MeV He\(^+\) ions from a Tandetron accelerator at a scattering angle 170° and the detector out-of-plane arrangement. The sample can be rotated around the \(\varphi\)- and \(\theta\)-axis in the small range of angles enabling to visualize the image scan of the planar channels and indicate the axial one in order to find some aligned RBS spectra.

With such an arrangement, we could perform additional investigations on selected irradiated films for a structural analysis focusing on the changes that occurred after Kr\(^+\) ion irradiation.

3. Results and discussions

Each film was irradiated 1, 2, 3 or 4 times marked respectively as Kr1, Kr2, Kr3 and Kr4 (given in table 1 and in the figures), with the ion fluences in the range of \(1.6 \times 10^{15}\text{–}1.9 \times 10^{16}\) ions cm\(^{-2}\) for Fe\(_3\)O\(_4\)/Fe(25-25 nm) and Fe\(_3\)O\(_4\)/Fe(100-50 nm), whereas for Fe\(_3\)O\(_4\)/Fe(50-50 nm) film we used higher ion fluxes in the range of \(6.7 \times 10^{15}\text{–}3.8 \times 10^{16}\) ions cm\(^{-2}\) (Kr4). Kr\(^+\) irradiations with similar ion fluences were performed on two single-layer film Fe\(_3\)O\(_4\)(25 nm) and Fe\(_3\)O\(_4\)/Fe(50 nm). The layer-thickness and composition of different layers of films in the as-grown state and after Kr\(^+\) ion radiation (by different ion fluences) estimated from RBS data analysis are given in table 1. We present only selected data revealing a visible effect of intermixing. In general, irradiations of the magnetite films by 1 MeV Kr\(^+\) ions induce a strong Fe–Mg intermixing leading to a large change in the layer composition and thickness and especially a formation of large interface zones. We present in figure 1 the comparison of RBS spectra in the as-grown state and after Kr\(^+\) ion irradiation for Fe\(_3\)O\(_4\)/Fe(50-50 nm) film, for which the ion beam mixing effect is most visible to eyes. We notice here that, not only single-layer magnetite film, but also bi-layer Fe\(_3\)O\(_4\) films exhibited a strong channeling effect set at untitled angle (\(\varphi = 0^\circ\)) observed even if by means of a standard RBS apparatus [37], when it happened that the incoming ion beam could go forwards along the channels formed along the main crystallographic (001) direction of magnetite, implying a large decrease of the backscattered signal in the RBS spectrum. For ensuring the randomness, most of RBS spectra were collected...
at tilted angle $\varphi = 10^\circ$. The RBS spectra of the as-grown film (figure 1) revealed a large Fe peak, a visible O peak ($O_{L1}$, from the (first) Fe$_3$O$_4$ surface layer (L1)) on a high background consisted of O step-edge ($O_{sub.}$) and Mg edge ($Mg_{sub.}$) from MgO substrate. The Fe peak is indeed consisted of a shoulder ($Fe_{L1}$) at the right-hand side of a Fe peak (the maximum, ($Fe_{L2}$)) attributed to the Fe signal respectively from the Fe$_3$O$_4$ layer (with an Fe content (~43%)) and from the Fe buffer layer (the second layer (L2) contained of 100% Fe). Since both layers consisted of Fe, the (backscattered) Fe signals are always overlapped. Increasing the thickness of the metallic Fe buffer layer would lead to their separation (distinction) in some extent. Moreover, the existence of such Fe layer would lead to a separation between the O signal from the Fe$_3$O$_4$ film ($O_{L1}$) and the large O signal ($O_{sub.}$) from MgO substrate. Our investigations have revealed that the minimal value for the Fe layer thickness should be 25 nm for obtaining such a separation, e.g. we observed a small but visible O peak in the RBS spectrum of Fe$_3$O$_4$/Fe(25-25 nm) film. Increasing the thickness of the Fe$_3$O$_4$ layer certainly would lead to an enhancement of the $O_{L1}$ signal and $Fe_{L1}$ signal revealed by e.g. an increase of the width of the O-peak and Fe-shoulder, as observed for Fe$_3$O$_4$/Fe(100-50 nm) film. We remind here again that by using the bi-layer structure, we could ensure to get the stoichiometric Fe$_3$O$_4$ layer on the film surface. The high guarantee of the stoichiometric Fe$_3$O$_4$ film was obtained in the case of the bi-layer films, when Fe layer blocks Mg diffusion into the Fe$_3$O$_4$ surface layer. The RBS data analysis provided the layer-thickness of (59–36 nm) for Fe$_3$O$_4$/Fe(50-50 nm) film, i.e. with a thicker Fe$_3$O$_4$ layer and a thinner Fe layer. Moreover, a wüstit-type (Fe$_{y}$Mg$_{1-y}$)O layer with a thickness of ~5 nm was formed at the Fe–MgO interface. In our previous study [36], we found out that, using a much shorter deposition time of the Fe$_3$O$_4$ layer and without using the post annealing, we were able to obtain the films with the Fe buffer layer with a thickness value close to the nominal one. The results gave a good proof that the top and bottom part of the Fe layer was oxidized during the film-growth. We notice here that SIMNRA analysis provides two different layers (spinel-type (Fe$_{1-x}$Mg$_x$)$_3$O$_4$ and wüstit-type (Fe$_y$Mg$_{1-y}$)$_x$O layer) at the film-substrate interface. However, for a simplicity, in table 1 as well as figures, we use a common (Fe,Mg)O$_y$ formula for addressing both interfacial layers since they consist of Fe, Mg and O. The only difference is the different composition of each element in the layer. The first irradiation (Kr1) with the ion fluence of $6.7 \times 10^{15}$ ions cm$^{-2}$ already induced a very strong mixing leading to a formation of the Fe$_3$O$_4$ layer at the Fe$_3$O$_4$–Fe interface and enhancement of the (Fe, Mg) O$_y$ layer (i.e. an increase of layer-thickness and Fe-content) at the Fe–MgO interface. Further irradiations implied much

**Figure 1.** The random (markers) and simulated (solid lines) RBS spectra of Fe$_3$O$_4$/Fe(50-50 nm) film grown on MgO(0 0 1) substrate after irradiations by 1 MeV Kr$^+$ ion beam. $O_{sub.}$ and $Mg_{sub.}$ Marked the O- and Mg-signal from MgO substrate. $O_{L1}$, $Fe_{L1}$ and $Fe_{L2}$ denoted the O- and Fe-signal from the (first) surface Fe$_3$O$_4$ layer and (second) Fe layer, respectively. For a clear view of ion beam mixing effect, we showed the full RBS spectra (both data and simulated ones) in a comparison with that in the as-grown state (a), the enlarged Fe peaks (b) and Fe–Mg background (c) with only simulated spectra for guiding of the eyes.
larger changes revealed by e.g. a much enhanced non-zero Fe–Mg background. Our data analysis indicated that, despite a large decreasing in the layer thickness, the bi-layer films still consisted of the pure Fe₃O₄-pure Fe layer structure after Kr3 irradiation (of 2.8 $\times$ $10^{16}$ ions cm⁻²). The pure Fe layer was found to disappear completely only after the fourth irradiation (Kr4) with the ion influence of 3.8 $\times$ $10^{16}$ ions cm⁻². In other words, such the Fe layer was oxidized completely forming the FeO₄ layer, as a consequence of intermixing. The crucial is that the stoichiometric Fe₃O₄ is well-preserved at this high ion fluence. For a clear vision of the Kr⁺ ion irradiation effect, we also included into figure 1 the comparison of the Fe signals and the non-zero background between Fe peak and Mg edge in an enlarged scale.

The bi-layer Fe₃O₄/Fe(25-25 nm) film exhibits a channeling effect, while no clear channeling effect was observed for bi-layer films with a total film thickness >50 nm. The normalized angular yield curve (with respect to the maximal backscattered yield of the random spectra (the channeling yield curve)) obtained from RBS-C experiments for Fe in the film for Fe₃O₄/Fe(25-25 nm) film was shown in figure 2. For a comparison, we included in the same figure the results for the single-layer film with a layer thickness of 10 nm [30] as well as MgO substrate. The MgO substrate exhibited a perfect crystal quality indicating by a small value of the minimum yield and the full width at half maximum (FWHM) for Mg, $\chi_{min}(\text{Mg})$ $\sim$ 2° and $\psi_{1/2}(\text{Mg})$ = 1.5°, respectively. For the 10 nm-thick single-layer magnetite film, a high crystallinity was exhibited with $\chi_{min}(\text{Fe})$ $\sim$ 20% and $\psi_{1/2}(\text{Fe})$ = 1.9° (for Fe in the film). The Fe₃O₄/Fe(25-25 nm) film has revealed one deep minimum ($\chi_{min}(\text{Fe})$ = 31°, $\psi_{1/2}(\text{Fe})$ = 1.4°) at a normalized tilted angle $\varphi$ = 0° and one minimum-shoulder feature ($\chi_{min}(\text{Fe})$ = 75%) attributed to the channeling respectively through the surface Fe₃O₄ layer and the Fe film beneath the surface layer. The difference in the angle between the two minima in the channeling yield curve is 2 degrees, attributed to the small difference in the orientation between the Fe atomic rows in the Fe layer and in the Fe₃O₄ layer. For bi-layer films with thicker thickness, the large lattice mismatch at both two interfaces (Fe₃O₄–Fe and Fe–MgO one), the formation of the interfacial layers, the displacements of the Fe rows etc have certainly led to a lowering of the crystallinity of the entire films, despite that each Fe₃O₄ and Fe layer can possess good atomic arrangements (i.e. each layer can exhibit a channeling effect).

The absolute values of the layer-thickness and density were determined from XRR measurements. In general, a good agreement for the layer thickness was obtained between RBS and XRR results. In all cases, the densities of the magnetite layers and Fe layers are found to be respectively $\rho$ (Fe₃O₄) = 5.2–5.4 g cm⁻³, $\rho$ (Fe) = 7.5–7.9 g cm⁻³, similar to those of the bulk density (5.21 g cm⁻³ and 7.87 g cm⁻³ for Fe₃O₄ and Fe, respectively), confirming the good stoichiometry of the films. We show in figure 3 the XRR results performed on Fe₃O₄/Fe(25-25 nm) and Fe₃O₄/Fe(50-50 nm) film. In the case of Fe₃O₄/Fe(25-25 nm) film, the layer thickness provided from the XRR analysis was in a reasonably good agreement with that of RBS one. However, two Fe layers with the same mass density but with different roughness were revealed. The Fe layer onto MgO substrate is very rough (with the estimated surface roughness of $r$ = 4 nm), while that beneath the Fe₃O₄ layer is quite smooth (r = 0.6 nm). We attributed such the large surface roughness to e.g. the large lattice mismatch between Fe and MgO (4%) during the first phase of Fe layer growth. Surprisingly, such the large lattice mismatch did not imply any roughness at the Fe₃O₄–Fe border. A sharp Fe₃O₄–Fe border line (no interface) was observed for Fe₃O₄/Fe(25-25 nm) film. For both Fe₃O₄/Fe(50-50 nm) and Fe₃O₄/Fe(100-50 nm) films, i.e. when the film-deposition time is twice or longer, XRR results revealed a thin interfacial layer (3–5 nm) between Fe₃O₄ and Fe layer with an estimated density of 6.0–6.2 g cm⁻³. It is certainly attributed to a mixed FeO–Fe layer (or Fe₃O₄ layer). The XRR measurements would not reveal e.g. the wüstite-type (Fe₃Mg₁₋ₓOₓ) layer at the film-substrate interface, since the density of such (mixed) layers was similar to that of MgO substrate (3.58 g cm⁻³).
We notice here that, despite of the fact that we could observe visible features in the RBS spectra, we should be careful in getting a reliable analysis in nm range, i.e. in the range of the depth resolution of a standard RBS method. On the other hand, both RBS and XRR results provided no evidence for an excess Fe within the Fe$_3$O$_4$ or for a stoichiometry gradient in the as-grown films. One might expect that growing the Fe$_3$O$_4$ film on an Fe buffer layer would lead to a film with excess interstitial Fe, but it is certainly not our case (for thick films). The excess Fe was found to exist, but only in a thin interfacial layer (3–5 nm) between Fe$_3$O$_4$ and Fe layer, and not in entire Fe$_3$O$_4$ film. Each bi-layer film indeed consists of the stoichiometric Fe$_3$O$_4$ and Fe layer. We found even no interface (within RBS and XRR resolution) in the Fe$_3$O$_4$/Fe(25-25 nm) film (as mentioned above).

Due to the formation of the mixed layers and large interface zone as a consequence of ion-induced intermixing, the films have no longer any clear layer-layer separation between different layers. Namely, Fe, O and Mg are present everywhere. (Mg is absent only in the stoichiometric Fe$_3$O$_4$ layer on the surface of the bi-layer films). The only difference between different layers or sub-layers is the difference in the element composition. However, the difference in the mass density of those mixed layers is small. Thus we could not obtain any reliable XRR results for irradiated films. Besides, the crystallinity is low and we were unable to obtain any reliable RBS-C results.

The pure Fe$_3$O$_4$ layer and the bi-layer structure of other films were found to survive under Kr$^+$ ion irradiation, although the layer thickness decreases largely (see table 1). The damage together with a large layer roughness, inhomogeneous mixed elements in the layer and between different layers, etc would certainly be the source of a large uncertainty of our RBS data-analysis for irradiated films. In other words, one should not trust completely the values themselves, but rather the meaning which they brought (the possible changes). Our investigations indicated that RBS measurements and data analysis provided a very clear picture of the ion mixing effect. We show in figure 4 the RBS spectra of three irradiated films after third or fourth irradiation. For a comparison, we show the normalized spectra and also the data for the single-layer Fe$_3$O$_4$(50 nm) film. For the Fe$_3$O$_4$(50 nm) as well as Fe$_3$O$_4$/Fe(25-25 nm) film, only one (overlapped) Fe peak was revealed, the ion beam mixing after the third irradiation was exhibited by a large decrease of the Fe peak intensity and a visible non-zero background between the Fe peak and Mg edge. For Fe$_3$O$_4$/Fe(100-50 nm) film, the distinguished Fe peak (maximum) and the wide shoulder feature were still observed after the fourth irradiation, indicating that the main bi-layer structure was still existed, despite that the layer thickness decreases largely. Namely, the layer-thickness remains as 63% and 69% respectively for Fe$_3$O$_4$ and Fe layer with respect to 100% as that in the as-grown state (table 1). No such distinguished Fe peak was observed for the film (3) under irradiation with a twice larger ion fluence.
peak was observed for Fe₃O₄/Fe(50-50 nm) after the fourth irradiation by a twice larger ion influence, since the pure Fe layer was no longer existed (or in other words the Fe layer was oxidized completely). The layer-thickness of Fe₃O₄ layer remains as 20%, while a value of 0% was found for Fe layer. For both those two films, a much larger non-zero background between the Fe peak and Mg edge was observed. Some small step-decreases were revealed attributed to a small deviation of element composition in different sub-layers (i.e. Fe redistribution into the MgO depth).

RBS and XRR data analysis for Fe₃O₄/Fe(100-50 nm) after (Kr⁴) irradiation provided three distinguished layers: Fe₃O₄ layer on the surface, the Fe layer and in between those two pure layers is the FeₓOᵧ layer (table 1). Since each layer has a large enough layer-thickness, we decided to perform additional RBS experiments with titled samples using a different RBS equipment on this irradiated film to look for a possible aligned RBS spectrum, despite of the fact that the film certainly has a low crystallinity. The results were shown in figure 5. The random RBS spectrum has revealed similar features as that collected by using the first RBS equipment revealing only Fe peak and a wide shoulder at the right hand side. By turning the sample, at a certain proper titled angle, we have observed a channeling effect through different layers. Namely, we obtained the aligned RBS spectrum exhibiting three peaks structure attributed to the three identified layers.

It is worth simulating the damage depth profiles induced by Kr⁺ ion irradiations. An energetic ion penetrating through a Fe₃O₄ and/or Fe generates vacancies in the Fe and O sublattices as well as Fe and O interstitials. The vacancies depth distribution in the particular layers can be evaluated by the Monte Carlo simulation of the ion interaction with matter using SRIM code [35]. Despite of the fact that SRIM theoretical calculations of atomic displacements take into account only ballistic processes and completely neglect dynamic ones as well as do not take into account crystallinity, SRIM simulations show the general trend and the damage propagation through the layers. In figure 6 we presented SRIM simulations with the full damage cascade for 1 MeV Kr⁺ ions in Fe₃O₄/Fe(100-50 nm) film revealing the Fe, O and Mg vacancies in the particular layers. We used the displacements energy in Kinchin–Peace model of 24 eV, 28 eV and 25 eV for Fe, O and Mg, respectively. The projected range of ion (R_p) is of 334 nm and the standard deviation is of about 96 nm. Fe and O vacancies illustrate the equal propagation of defects via Fe and O atoms knocking in the Fe₃O₄ matrix. We notice an increase of vacancies in the Fe layer attributed to a higher density of this layer (i.e. to an increase of the number of atoms per length of the ion trajectory and of energy stopping). Besides, the Fe vacancies depth profile in Fe buffer layer has the same shape as that we observed in the RBS spectrum in figure 5, taking into account the fact that SRIM included two layers only (Fe₃O₄(100 nm) and Fe(50 nm)) and not FeₓOᵧ intermixed layer created during the irradiation. The O and Fe vacancies depth profile in the first layer has in fact the same shape, thus are not recognizable in the figure 5, but it can be deduced from the total vacancies depth profiles, that the total number of vacancies is about twice higher as the sum of Fe and O vacancies.

For a clear illustration of the ion beam mixing effect, i.e. the change in the composition and thickness of the layers, we show in figure 7 the film diagram before and after (selected)
irradiations. We draw the layer thickness in a millimeter scale while keeping the same proportional portion with respect to the values estimated from SIMNRA in nm for different layers of the films (see table 1). The original separation (i.e. in the as-grown state) between the film and MgO substrate is indicated by the solid lines. Different colours indicate different layer compositions. In order to have a good view regarding the change of the layer thickness and composition, we show only the main layers. For instance, we presented only one mixed Fe3O4 layer, although the RBS data analysis provided that such a layer consisted of several sub-layers with a small deviation of x- and/or y-component. Besides, we used the straight lines to show the real values of the estimated layer thickness of the mixed layers deeply into the MgO substrate, while for a large layer-thickness of the mixed layers we show the reduced thickness presented by curved lines. It shows clearly that the pure Fe3O4 layer in all investigated bi-layer films were well-preserved, while that for the single layer films could not survived under 1 MeV Kr+ ion irradiations.

The dependence of the relative changes of the layer thickness (in %) with increasing Kr fluence is shown in figure 8. As we mentioned earlier, irradiation with Kr fluence below 1015 Kr cm−2 did not lead to any visible change in the RBS spectra. However, the relative layer thickness was found to decrease rapidly upon Kr fluence higher than 1016 Kr cm−2. The ion fluence upon which the Fe buffer layer disappeared determined experimentally was 3.8 × 1016 Kr cm−2. From a polynomial fits through the data points, the stoichiometry of the surface Fe3O4 layer is expected to be destroyed (i.e. the composition is changed into Fe2O3, i.e. x = 3, y = 4) upon irradiation with a larger fluence >5.0 × 1016 Kr cm−2.

4. Conclusions

Our investigations showed that the stoichiometry of the Fe3O4 layer on the surface of the bi-layer film (the magnetite-on-Fe film) is well preserved under 1 MeV Kr+ ion irradiation at a large ion fluence ϕ = 3.8 × 1016 ions cm−2, indicating a high stability of magnetite layer in external conditions such as Kr+ ion irradiation. This information is crucial for using the magnetite-based devices in spintronics. Besides, the bi-layer structure (Fe3O4/Fe film-structure) was also preserved under ion irradiation with lower ion fluencies.

1 MeV Kr+ ion irradiation has induced a large interfacial zone resulting in a more than double thickness of the films. It indicates a possibility of using the high-energy ion beam in controlled experiments for tailoring of the magnetite films and their interface engineering to obtain the layers or the interfaces with required thickness and desired properties for the practical applications.

Acknowledgments

The magnetite thin films were prepared within the scope of cooperation with Prof J Korecki (AGH Kraków). We highly acknowledge the fruitful cooperation with RBS group in the Institute of Nuclear Physics of the University Frankfurt/Main during performing RBS and RBS-C experiments.

References

[1] Tsuda N, Nasu K, Yanase Y and Siratori K 1990 Electronic Conductions in Oxides vol 94, ed M Cardona et al (Berlin: Springer)
[2] Subias G, Garcia J and Blasco J 2005 Phys. Rev. B 71 155103
[3] Piekarz P, Parlinski K and Oles A M 2007 Phys. Rev. B 76 165124
[4] Lorenzo J E, Mazzoli C, Jaouen N, Detlefs C, Mannix D, Grenier S, Joly Y and Marin C 2008 Phys. Rev. Lett. 101 226401
[5] Fong C Y, Pask J E and Yang L H 2013 Half-Metallic Materials and Their Properties (Materials for Engineering) vol 2 (London: Imperial College Press)
[6] Arras R, Calmens L and Warot-Fonrose B 2016 Appl. Phys. Lett. 100 032403
[7] Fonin M, Pentcheva R, Dedkov Yu S, Sperlich M, Vyalikh D V, Scheffler M, Rüdiger U and Güntherodt G 2005 Phys. Rev. B 72 104436
[8] Tobin J G, Morton S A, Yu S W, Wadid Gill D G, Schuller I K and Chambers S A 2007 J. Phys.: Condens. Matter 19 315218
[9] van der Zaag P J, Bloemen P J H, Gaines J M, Wolf R M, van der Heiden P A A, van de Veerdonk R J M and de Jonge W J M 2000 J. Magn. Magn. Mater. 211 301
[10] Coey J M D, Berkowitz A E, Balcells L I, Putnis F F and Parker F T 1998 Appl. Phys. Lett. 72 734
[11] Ziese M and Blythe H J 2000 J. Phys.: Condens. Matter 12 13
[12] Prakash T, Williams G V M, Kennedy J and Rubanov S 2016 J. Appl. Phys. 120 123905
[13] Kim W, Kawaguchi K, Koshizaki N, Sohma M and Matsumoto T 2003 J. Appl. Phys. 93 8032
[14] Wu H-C et al 2015 Sci. Rep. 5 15984
[15] Kim D K, Zhang Y, Voit W, Rao K V, Keh J, Bjelke B and Muhammed M 2001 Sc. Mater. 44 1713
[16] Umo G, Gunduz U, Oprea O, Ficai D, Sonmez M, Radulescu M, Alexie M and Ficai A 2015 Curr. Top. Med. Chem. 15 1622
[17] Wang X et al 2007 J. Biomedical Mater. Res. A 80A 852
[18] Mürbe J, Rechtenbach A and Töpfer J 2008 Mater. Chem. Phys. 110 426
[19] Parkinson G S 2016 Surf. Sci. Rep. 71 272
[20] Hendrich V E and Cox P A 1994 The Surface Science of Metal Oxides (Cambridge: Cambridge University Press)
[21] Kung H H 1989 Transition metal oxides: surface chemistry and catalysis Studies in Surface Science and Catalysis vol 45 (Amsterdam: Elsevier)
[22] Wang W et al 2013 Phys. Rev. B 87 085118
[23] Parkinson G S, Diebold U, Tang J and Malkinski L 2012 Tailoring the Interface Properties of Magnetite for Spintronics in Advanced Magnetic Materials ed L Malkinski (Intech Publisher) chapter 3
[24] Bliem R et al 2014 Science 346 1215
[25] Chamber S A 2000 Surf. Sci. Rep. 64 105
[26] Korecki J, Handke B, Spiridis N, Slezak T, Flis-Kabulska I and Habel J 2002 Thin Solid Films 412 14
[27] Spiridis N, Barbasz J, Łodziana Z and Korecki J 2006 Phys. Rev. B 74 155423
[28] Davis E M, Zhang K, Cui Y, Kuhlenbeck H, Shaikhutdinov S and Freund H J 2015 Surf. Sci. 636 42
[29] Kim-Ngan N-T H, Balogh A G, Meyer J D, Brötz J, Hummelt S, Zajac M, Slezak T and Korecki J 2008 Surf. Sci. 602 2358
[30] Kim-Ngan N-T H, Balogh A G, Meyer J D, Brötz J, Zajac M, Slezak T and Korecki J 2009 Surf. Sci. 603 1175
[31] Kim-Ngan N-T H, Balogh A G, Meyer J D, Brötz J, Zajac M, Slezak T and Korecki J 2009 Nucl. Instrum. Methods Phys. Res. B 267 1484
[32] Kumara R, Khan M W, Srivastava J P, Arora S K, Sofin R G S, Choudhary R S and Shvets I V 2016 J. Appl. Phys. 100 033703
[33] Sun J R, Wang Z G, Wang Y Y, Zhu Y B, Pang L L, Shen T L and Li F S 2016 Nucl. Instrum. Methods Phys. Res. B 269 277
[34] Zajac M, Freindl K, Ślęzak T, Ślęzak M, Spiridis N, Wilgocka-Ślęzak D and Korecki J 2011 Thin Solid Films 519 5588
[35] Ziegler J F, Ziegler M D and Biersack J P 2010 Nucl. Instrum. Methods B 268 1818
[36] Mayer N 2014 Nucl. Instrum. Methods Phys. Res. B 332 176
[37] Kim-Ngan N-T H 2010 Adv. Nat. Sci. I 045010
[38] Anderson J F, Kuhn M, Diebold U, Shaw K, Stoyanov P and Lind D 1997 Phys. Rev. B 56 9902
[39] Voogt F C, Fujii T, Smulders P J M, Niesen L, James M A and Hibma T 1999 Phys. Rev. B 60 11193
[40] Ruby C, Humbert B and Fusy J 2000 Surf. Interface Anal. 29 377