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Citation: Journal of Applied Physics **115**, 17B907 (2014); doi: 10.1063/1.4868704
View online: http://dx.doi.org/10.1063/1.4868704
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/115/17?ver=pdfcov
Published by the AIP Publishing

Magnetization control for bit pattern formation of spinel ferromagnetic oxides by Kr ion implantation

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(Presented 7 November 2013; received 23 September 2013; accepted 26 December 2013; published online 20 March 2014)

As a first step toward the development of bit-patterned magnetic media made of oxides, we investigated the effectiveness of magnetism control by Kr implantation in a typical spinel ferromagnetic oxide, Fe_3O_4. We implanted Kr ions accelerated at 30 kV on 13-nm-thick Fe_3O_4 thin films at dosages of $(1–40) \times 10^{14}$ ions/cm^2. Magnetization decreased with increase in ion dosages and disappeared when irradiation was greater than 2×10^{15} ions/cm^2 of Kr ions. These dosages are more than ten times smaller than that used in the N_2 implantation for metallic and oxide ferromagnets. Both the temperature dependence of magnetization and the Mössbauer study suggest that the transition of Fe_3O_4 from ferromagnetic to paramagnetic took place sharply due to Kr ion irradiation, which produces two-phase separation—ferromagnetic and nonmagnetic with insufficient dosage of Kr ions. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4868704]

I. INTRODUCTION

Because of the increasing demand for high-density recording devices, perpendicular magnetic recording systems have emerged as the predominant hard disk system. Further increasing the storage density in these devices requires a decrease in the physical volume required for one stored bit, but this is difficult because of superparamagnetic effects that emerge in magnetic media at small dimensions. One method for overcoming this limit is the use of bit patterned media (BPM).[1,2] In BPM, the recording bits are magnetically separated in structures that are spatially well defined, i.e., patterned. These arrays of nanostructures/patterns are typically fabricated using techniques such as lithography with bit-patterned masks, the imprint technique,[1] or ion implantation. Ion implantation, when applied to a magnetic material,[3] can alter the materials magnetic character, either from ferromagnetic to nonmagnetic[4,5] or from nonmagnetic to ferromagnetic.[6] This technique obviates the fill-back process required in other lithographic methods.

In previous studies, metallic perpendicular-magnetic anisotropic (PMA) media comprising Co/Pd multilayers[4] and CoCrPt (Refs. 4 and 5) were investigated as possible substrates for bit-patterning, and nonmagnetic states were introduced by irradiation with N_2 ions at 6×10^{16} ions/cm.[4] Kr ions are also effective in controlling magnetism in metallic $CoPt_3$ and MnGe.[7,8] Though nitrogen irradiation is effective for fabricating metallic PMA systems, there are significant advantages to the use of Kr ions, such as lower required dosages and reduced lateral damage related to Kr's higher mass.

Oxide ferro-/ferrimagnetic materials have been investigated for many years and have tremendous potential for use in various applications[9] such as high-density recording media[10] and spintronic devices.[11] Recently, we fabricated spinel-type oxide thin films using RF sputtering[12] and found strong PMA energy on the order of 10 Mergs/cm^3 in Co ferrite thin films grown on MgO(001) substrates.[10] These materials have potential as magnetic recording media, and it would be beneficial to develop techniques for patterning this material, as well. Previously, we demonstrated the effectiveness of N_2 ion implantation in magnetization control in these materials.[13] In this paper, we report our efforts to control the magnetization of the "typical" spinel ferromagnetic oxide, Fe_3O_4, using Kr ion irradiation. Gathering these results is the first step toward the synthesis of nanopatterned oxide magnetic materials for use in storage devices.

II. EXPERIMENTAL PROCEDURE

We prepared Fe_3O_4 thin films using reactive O_2 sputtering during film growth in an RF planar magnetron sputtering apparatus.[12] We used cleaved MgO(001) single crystals as substrates. Our 13 nm thick films were sputter-deposited at a substrate temperature of 300 °C. For the Mössbauer studies, we custom-made a thin, annular tablet with a thickness of 1 mm out of 25% enriched ^{57}Fe and placed it over the erosion region of a natural Fe sputter target. Using this ^{57}Fe-enriched target system, we fabricated ferrite thin films with a thickness range of 11–13 nm in the same manner as the other samples. Details of sample preparation and characterization are described in a previous study.[12]

We used the Fe_3O_4 films coated with and without a carbon layer of around 10 nm prior to ion irradiation to control the efficiency of accelerated ions. Kr ion irradiation was conducted in a conventional ion implantation apparatus. We set

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the acceleration voltage (V_{acc}) to 30 kV and controlled the ion dose in the range of (1–40) $\times 10^{14}$ ions/cm^2. We confirmed that these conditions were suitable using the SRIM simulation software. The Fe content in the films both before and after irradiation was measured using X-ray fluorescence spectroscopy (XRF). Magnetization measurements were carried out by vibration sample magnetometry (VSM), and the temperature-dependence of the magnetization using a SQUID-VSM magnetometer. The Mössbauer study was performed using standard conversion electron Mössbauer spectroscopy.

III. RESULTS AND DISCUSSION

Transmission electron micrographs (TEMs) of an Fe_3O_4 thin film after Kr ion irradiation of 2×10^{15} ions/cm^2 are in Fig. 1. We found that the carbon coating remained with the as-coated thickness >10 nm. In the associated diffraction pattern (not shown), we observed that there are cubic crystallites in the Fe_3O_4 layer. Fig. 1(b) is a high magnification TEM of the same film as in Fig. 1(a), and it still shows the lattice structure. We estimate that the size of the grains is 2–3 nm from the image, which is smaller than that of the as-deposited films.[12]

The magnetization curves for the Kr-implanted films are in Fig. 2. The saturation magnetizations decreased with increase in dosage and almost vanished at the Kr ion irradiation dosage of 2–4 $\times 10^{15}$ ions/cm^2. The saturation magnetization is plotted against the dosage in Fig. 3, together with the corresponding data for N_2 irradiation.[13] It decreases with the increase in dosage and reaches almost zero at dosage of 2×10^{15}, which is much smaller than the value for N_2 ion irradiation, 6×10^{16} ions/cm^2. The Fe content estimated from XRF data was almost constant through the Kr ion implantation. This decrease in magnetization produced by Kr irradiation is not a result of a decrease in Fe content but because of a structural change in the film. Additionally, coercive force increased from 100 Oe to 280 Oe with an increase

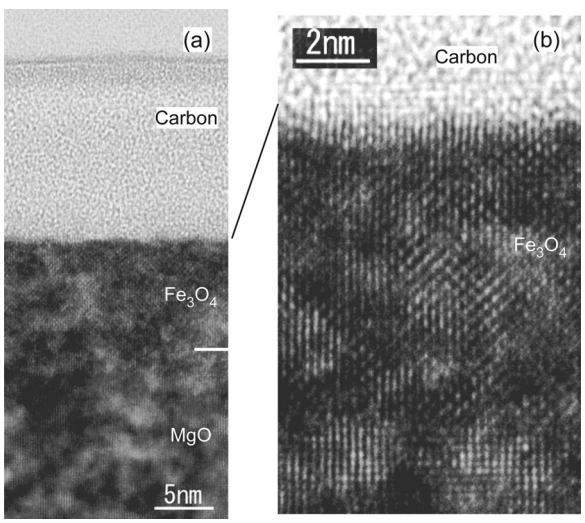

FIG. 1. TEMs of a cross section of a Fe_3O_4 thin film irradiated with Kr ions (30 kV, 2×10^{15} ions/cm^2). In the low magnification image (a), the boundaries between the carbon layer–Fe_3O_4 and Fe_3O_4–MgO regions are clearly seen.

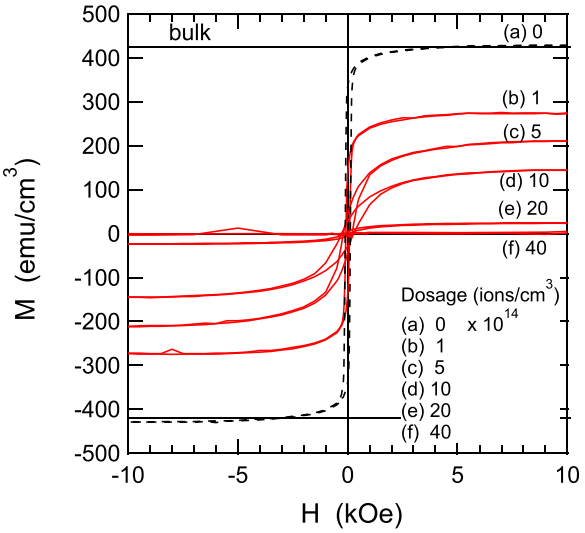

FIG. 2. Magnetization curves for the Kr ion-implanted Fe_3O_4 thin films produced with $V_{acc} = 30$ kV. The dosages were (a) 0, (b) 1×10^{14}, (c) 5×10^{14}, (d) 10×10^{14}, (e) 20×10^{14}, and (f) 40×10^{14} ions/cm^3. The straight solid line shows the amplitude of the bulk saturation magnetization for Fe_3O_4.

of the dosage and then decreased. It suggests that the ferromagnetic parts began to separate and form small grains due to the increase of nonmagnetic parts and tended to show magnetic characteristics of single domain particles.

The magnetization vs. temperature curves for the Kr-ion-irradiated Fe_3O_4 thin film samples are in Fig. 4. These suggest that the ferromagnetic components in the ion-implanted films have an almost uniform magnetic transition temperature throughout the layer, similar to the N_2-implanted case.[13] Our TEM observations support the evidence for this similarity in their microstructure.

The Mössbauer spectra of the Fe_3O_4 thin films with Kr-irradiation treatments of (b) 2×10^{15} and (c) 4×10^{15} ions/cm^2 are in Fig. 5. The film thicknesses are 11 and 13 nm, respectively. Magnetization levels of 200 and 0 emu/cm^3 were achieved for samples (b) and (c), respectively. The former

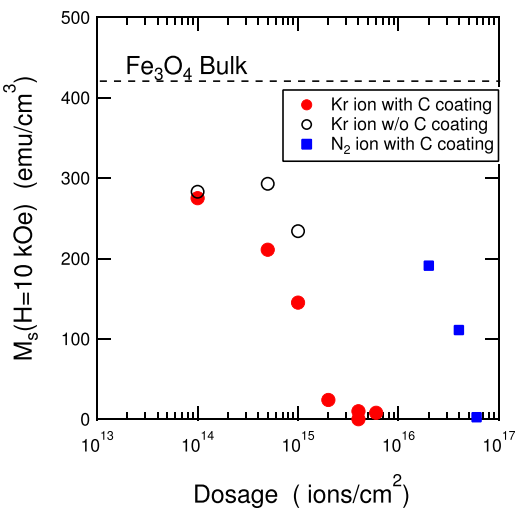

FIG. 3. Influence of Kr ion implantation on saturation magnetization, M_s, of three Fe_3O_4 sputtered thin films. Solid circles and open circles show the magnetization for the samples with C coated and without C coated layer, respectively. Closed squares show the magnetization of the sample with C coated layer irradiated by N_2 ions.[13]

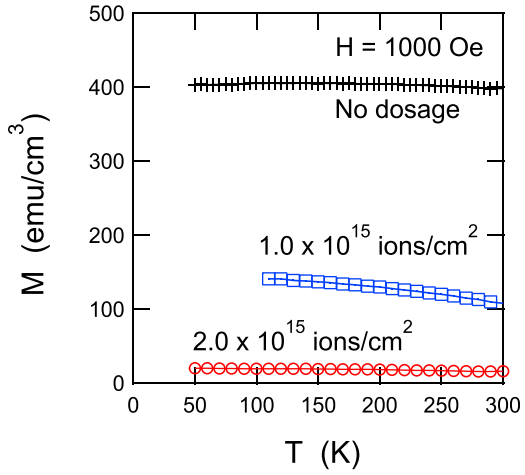

FIG. 4. Temperature dependence of magnetization in Kr-implanted Fe_3O_4 thin films with $V_{acc} = 30$ kV at 1 kOe.

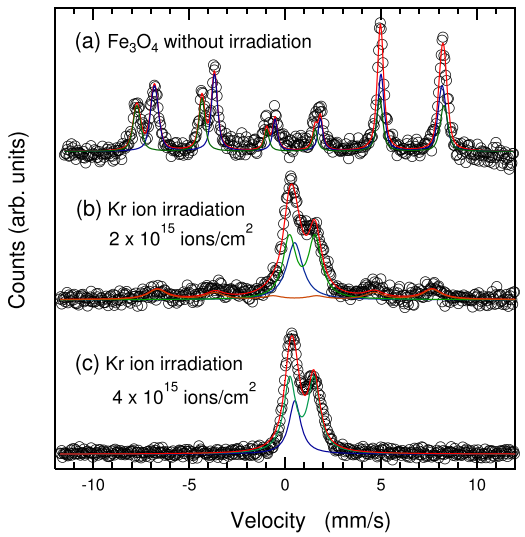

FIG. 5. Mössbauer spectra of Fe_3O_4 thin films, (a) an as-prepared films with a thickness of 50 nm, Kr-implanted films (b) with an 11 nm thickness after irradiating at 2×10^{15} ions/cm^2, and (c) with a 13 nm thickness after irradiating at 4×10^{15} ions/cm^2. Solid lines show the fits used to decompose the spectra.

amplitude of magnetization is higher than the value listed in Fig. 2, perhaps due to the sample thickness. The spectrum for a 50 nm thick Fe_3O_4 film without irradiation is plotted as a reference in Fig. 5(a) and was fitted to the combination of two magnetic subspectra with bulk parameters. The spectrum of the low-irradiation sample in (b) was fitted to the combination of a weak broad magnetic sextet, a non-magnetic doublet, and a non-magnetic singlet. The ferromagnetic component has a hyperfine field of 445 kOe and an isomer shift of 0.50 mm/s which are almost comparable to those of Fe^{3+} ions and wide line widths. The area ratio of a ferromagnetic component is roughly estimated to be 23%, and this agrees qualitatively with the value of saturation magnetization.

A further increase in irradiation ions resulted in the disappearance of the ferromagnetic component of (b), and the paramagnetic components can be fitted by using the same parameters as those for sample (b). There are no intermediate subspectra with smaller hyperfine fields than those shown in the spectra of (a). Our results imply two-phase separation and absence of any intermediate phase in the irradiated sample, thereby suggesting that the transition of Fe_3O_4 from ferromagnetic to paramagnetic occurred sharply due to Kr ion irradiation. This result is consistent with the fact that lower temperature-dependent magnetization levels were observed in the ion-implanted samples.

ACKNOWLEDGMENTS

The authors would like to express their thanks to Professor J. Inoue and Dr. A. Kikitsu for fruitful discussions. We would also like to thank Dr. Takahashi, Dr. Furubayashi, and Dr. Mitani at National Institute of Materials Science for help with the magnetization measurements. Kr ion irradiation was performed at Nagoya University with the support of Nanotechnology Platform. Mössbauer studies were performed at Tandem Accelerator Complex, University of Tsukuba. This work was supported by the Element Science and Technology Project, MEXT, Japan.

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