Crystal structure transformation of Fe_3O_4 from spinel type to rock salt type via ion irradiation

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Introduction

An interesting topic of recent study is how spinel materials, such as $MgAl_2O_4$, $MgGa_2O_4$ and $MgIn_2O_4$[1], are affected by ion implantation, a technique which can change a material's fundamental properties. However, hardly any investigation has been carried out on irradiated spinel ferrite materials. In the previous study, we investigated the effect of Kr ion implantation on the epitaxial $CoFe_2O_4$ thin films, and found that the magnetization decreased due to ion irradiation causing a structural transformation from spinel to rock salt type. However, the mechanism of topotactic reaction in epitaxial films was not well explained. In this study, we focus on prototype spinel Fe_3O_4 thin films and investigate the structural transformation from spinel to rock salt via Kr ion implantation.

Experiment

An epitaxial Fe_3O_4 thin film with a thickness of 16 nm was grown on MgO (001) single crystal substrates by reactive RF sputtering. Kr ions were accelerated in a conventional ion implantation system in Nanotechnology Platform. The acceleration was set at 30 keV and the ion dosage was controlled at 5×10^{15} ions/cm^2. A ^{57}Fe enriched tablet with an annular shape was embedded to a natural Fe sputtering target to perform room temperature conversion electron Mössbauer spectroscopy (CEMS). The crystal structures were determined by X-ray diffraction at beamline BL-4C of the Photon Factory, KEK, while the magnetization was measured by vibrating sample magnetometer (VSM) at room temperature. The cross-section images of the both pre- and post-irradiation films were taken by a scanning transmission electron microscope (STEM).

Results

Figure 1 and Figure 2 show annulus dark-field (ADF) STEM images and their electron diffraction pattern of thin film at as grown Fe_3O_4 and ion irradiated one, respectively. Comparing to electron diffraction patterns before and after ion irradiation, we observed Fe_3O_4 with spinel structure in Fig.1, and in Fig.2 after ion irradiation the electron diffraction pattern changed, and it should be rock salt structure, which is consistent with the results from XRD.

From the RBS measurement (not shown), we obtained that the Fe component had no change after ion irradiation. The ADF-STEM images indicate that a tiny decrease of thickness after ion irradiation less than 1 nm. As a result, we consider that after ion irradiation, spinel structure of Fe_3O_4 transformed to rock salt structure of Fe_xO (x=0.75), almost maintained Fe:O=3:4 which could be a non-equilibrium phase of Fe-O.

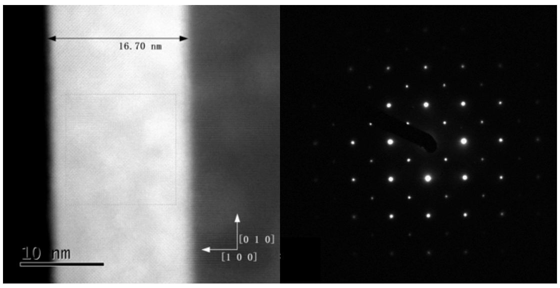

Fig. 1. The STEM image and electron diffraction pattern of Fe_3O_4 thin film as grown.

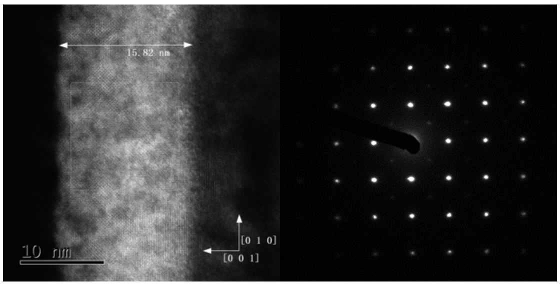

Fig. 2. The STEM image and electron diffraction pattern of Fe_3O_4 thin film after 5×10^{15} ions/cm^2 ion irradiation.

1) B.P. Uberuga *et al., Nat. Commun.*, 6 (2015)