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Defect induced modification of structural, topographical and magnetic properties of zinc ferrite thin films by swift heavy ion irradiation

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ABSTRACT

Swift heavy ion irradiation provides unique ways to modify physical and chemical properties of materials. In ferrites, the magnetic properties can change significantly as a result of swift heavy ion irradiation. Zinc ferrite is an antiferromagnet with a Neel temperature of 10 K and exhibits anomalous magnetic properties in the nano regime. Ion irradiation can cause amorphisation of zinc ferrite thin films; thus the role of crystallinity on magnetic properties can be examined. The influence of surface topography in these thin films can also be studied. Zinc ferrite thin films, of thickness 320 nm, prepared by RF sputtering were irradiated with 100 MeV Ag ions. Structural characterization showed amorphisation and subsequent reduction in particle size. The change in magnetic properties due to irradiation was correlated with structural and topographical effects of ion irradiation. A rough estimation of ion track radius is done from the magnetic studies.

1. Introduction

Design and fabrication of new materials with novel properties is one of the main objectives of material scientists. Material scientists adopt a wide variety of processing techniques to produce such materials. One such technique is to modify the material properties by subjecting the material to ion irradiation. Ion beams can be employed for synthesis, modifications and characterization of materials. When ions traverse through a material, ions can impart their energy and momentum to the material. Depending on the energy of ions, two regimes can be defined viz, nuclear energy regime (∼below 10 keV/amu) and electronic energy regime (∼greater than 100 keV/amu). Slow energetic ions lose energy mainly via nuclear energy loss while high energetic ions lose energy via electronic energy loss. Ions can pass through the material when the range of ions is greater than the thickness of the material. Swift heavy ions can cause amorphisation, recrystallisation and nanostructuring in materials [1–2].

The formation of ion tracks by swift heavy ions depends on both the material properties and the energy of incoming ion [3]. Track formation occurs beyond a particular threshold of electronic energy loss, track size can be controlled by ion energy and fluence [3,4]. The formation of ion tracks can greatly influence magnetic properties as the stress generated by the tracks can affect anisotropy and permeability [5–7]. Ion induced modifications of ferrites has been studied extensively by researchers [3,6,8–11]. Ferrites are an important class of material having spinel, inverse spinel or mixed spinel structure. The magnetic properties are structure sensitive and the degree of structural disorder determines the magnetic order. In a normal spinel structure represented by $M_A^{2+}Fe_{2B}^{3+}O_4^{2-}$, the divalent cation M occupies the tetrahedral vacancy (A site) and the trivalent cation occupies the octahedral vacancy (B site). The interaction of ions in A and B site of the spinel structure leads to J_{AB} interaction giving rise to ferrimagnetic ordering while J_{AA} and J_{BB} lead to antiferromagnetic ordering. Small structural deviation can induce glassy behaviour. The threshold electronic energy loss for track formation in ferrites is 20 keV/nm [12]. Many studies have been carried out on ion induced modification in inverse and substituted ferrites which are already ferrimagnetic [5,8,11]. In nickel zinc ferrite ($Ni_{0.65}Zn_{0.375}In_{0.25}Ti_{0.025}Fe_{1.70}O_4$) and magnesium zinc ferrites ($Mn_{0.75}Zn_{0.18}Fe_{2.07}O_4$), ions are reported to cause structural and magnetic deviation [8,11].

Zinc ferrite ($ZnFe_2O_4$) is a normal spinel and exhibits antiferromagnetic properties in the bulk [13]. However, thin film and nano forms of zinc ferrite exhibit altogether different properties and this has been attributed to cation redistribution [14–19]. Shenoy et al. have observed room temperature superparamagnetic behaviour in

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ball milled zinc ferrite [14]. Hoffmann et al. observed glassy behaviour in nano zinc ferrite, the blocking temperature was found to be influenced by particle size [20]. Jeong et al. reported that nanocrystalline zinc ferrite exhibited ferrimagnetism up to 460 K and co-existent ferrimagnetic and antiferromagnetic ordering at 10 K. The competition between Fe ions among A and B sites to interact via J_{AB} and J_{BB} results in canted spin structure of Fe ions in B site [21]. Nakashima et al. have reported high magnetisation in zinc ferrite thin films prepared by RF sputtering [15]. Bohra et al. have studied the properties of zinc ferrite thin films prepared by RF sputtering and Pulsed Laser Deposition (PLD) [19]. Recently, Liang et al. have observed a magnetisation of 1 memu/cc in zinc ferrite thin films [22]. Authors of this paper have reported a magnetisation of 18 emu/cc at room temperature in zinc ferrite thin films of thickness 120 nm prepared by RF sputtering [23]. The altogether different properties of zinc ferrite, which depends mainly on cation redistribution, make zinc ferrite an interesting candidate for research. The effect of amorphisation induced by SHI in zinc ferrite thin films has not yet been studied and is the objective of this investigation. The defects and changes in surface morphology induced as a result of irradiation, which can alter the magnetic properties, is also interrogated in this study.

2. Experimental

Zinc ferrite thin films were prepared by RF sputtering from a phase pure target synthesized by sol gel auto combustion method. The films were deposited on naturally oxidized Si substrates at an RF power of 150 W for 90 min. Cross sectional TEM operated at 200 kV in the imaging mode is used to determine the film thickness. The films were annealed at 600 °C and then irradiated using 100 MeV Ag ions at fluences of 1×10^{12}, 1×10^{13} and 3×10^{13} ions/cm^2. The irradiation was performed using 15 UD Pelletron accelerator at Inter University Accelerator Centre, New Delhi. The range and energy loss of 100 MeV Ag ions in zinc ferrite films were simulated using the SRIM code [24]. The electronic energy loss of 100 MeV Ag ions in zinc ferrite, as calculated, was 16 keV/nm (Fig. 1). The range of ions was 11 μm. Structural characterization was done using a Glancing Angle X Ray Diffractometer (GXRD) Bruker Discover D-8 with Cu Kα (λ = 1.5406 Å) at a glancing angle of 1^0. The crystallite size D is calculated using the Scherrer formula $D = \frac{0.9\lambda}{\beta \cos\theta}$, where λ is the wavelength of X rays used, β full width at half maximum and θ is the diffraction angle. Atomic Force Microscope (AFM) Nanoscope IIIa Digital Instruments, Veeco was employed to study the morphological evolution of sample with ion irradiation. Roughness and Power Spectral Density (PSD) were deduced from AFM images. Magnetic studies were carried out with a 7T SQUID VSM. M-H curves at room temperature and at 5 K were recorded. Field Cooled-Zero Field Cooled (FC-ZFC) measurements were performed from 300 K to 5 K at a cooling field of 50 Oe and 100 Oe.

3. Results and discussion

The film thickness calculated from cross sectional TEM (Fig. 2) was found to be 320 nm. The range of ions is greater than film thickness, so the ions pass through the film and get terminated in the substrate.

The GXRD images of pristine and irradiated films are shown in Fig. 3. Each sample was subjected to GXRD before and after irradiation to avoid sample to sample variation. The crystallite size calculated using the Scherrer formula, was found to be 21 nm for pristine film. The crystallite size varied with ion fluence. At a fluence of 1×10^{12} ions/cm^2, crystallite size reduced to 15 nm and on irradiation at highest fluence of 3×10^{13} ions/cm^2 crystallite size increased to 17 nm. The decrease in crystallite size with ion fluence has been observed in many systems and is explained on the basis of amorphisation of the material on irradiation [8,25]. The amorphisation of the crystalline material can be explained by the thermal spike model; the high energy imparted by ions creates localized high temperature zones (10^5 K) along the ion path, which can melt the material, this is followed by sudden cooling ($\sim 10^{-13}$ ps) resulting in amorphisation along the ion path [26,27]. However, in our study complete amorphisation have not taken place. The high energy imparted can also cause break up of crystallites. These crystallites can flow along the melted track and rejoin to form larger crystallite. The observed increase in crystallite size at higher fluence is attributed to aggregation of these broken crystallites [28]. This is further evident from the AFM analysis discussed in the following section.

The 2D and 3D AFM images are shown in Figs. 4 and 5. The grain size was observed to decrease at lower fluence and increase at highest fluence, consistent with the GXRD studies. For the 3×10^{13} ions/cm^2 irradiated samples one can observe agglomeration of grains, resulting in increase in grain size.

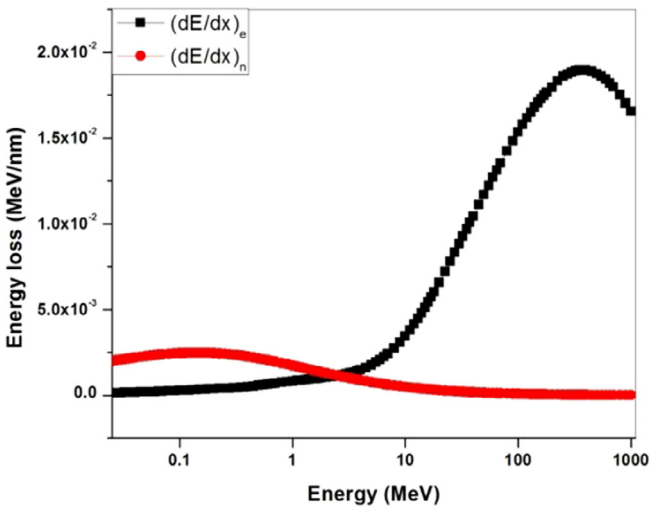

Fig. 1. SRIM simulation of electronic and nuclear energy loss of Ag ions in zinc ferrite.

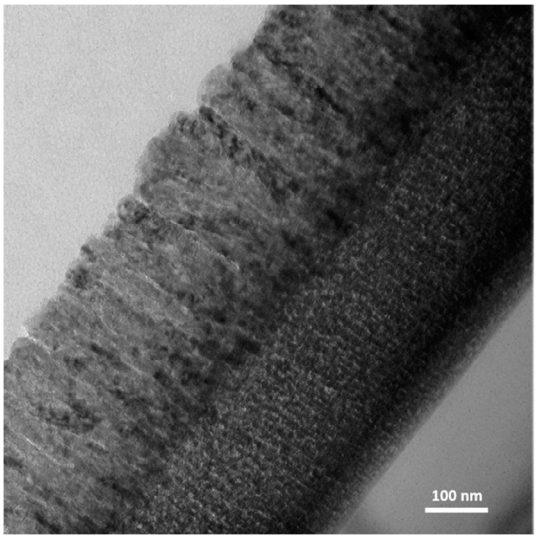

Fig. 2. Cross sectional TEM image of pristine zinc ferrite film.