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Room temperature ferrimagnetism and low temperature disorder effects in zinc ferrite thin films

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ABSTRACT

Zinc ferrite is a normal spinel and antiferromagnetic in nature with a Neel temperature of 10 K in the micron regime. It exhibits interesting features like superparamagnetism, spin glass and ferrimagnetism in the nano-regime. These anomalies make zinc ferrite striking among various other spinels. Further, in the thin film form, the magnetic properties are dependent on preparative techniques, annealing and deposition parameters. In the present work, zinc ferrite thin films were prepared by RF sputtering. The films were annealed at 400° C and 600° C. The thickness and composition of films were estimated by employing Rutherford Backscattering Spectrometry (RBS). The structural and microstructural studies conducted using Glancing X Ray Diffractometer (GXRD) and Transmission Electron Microscope (TEM) indicates the formation of a spinel phase and grain growth was observed with annealing. Magnetic measurements were carried out using a Superconducting Quantum Interferometer Device–Vibrating Sample Magnetometry (SQUID VSM). The films were found to be ferrimagnetic at room temperature and Field Cooling–Zero Field Cooling (FC–ZFC) studies indicate the presence of disorders.

1. Introduction

Zinc ferrite is a classical example of an antiferromagnet with a Neel temperature of 10 K [1]. In the micron regime it exhibits a normal spinel structure with Zn^{2+} ions having exclusive tetrahedral site (A site) preference while Fe^{3+} ions occupy the octahedral sites (B site) in an fcc close packed oxygen sub-lattice and is represented by $Zn_A^{2+}Fe_{2B}^{3+}O_4{}^{2-}$. The antiferromagnetism exhibited by zinc ferrite is attributed to weak J_{BB} interaction. There are reports where normal spinel zinc ferrite is not an antiferromagnet but a three dimensional spin frustrated magnet [2].

In the nano-regime zinc ferrite exhibit anomalous magnetic behavior, in that it is purported to exhibit ferrimagnetism, spin glass, superparamagnetism or spin cluster behavior. This anomaly has been attributed to cation redistribution where in some amount of Zn^{2+} ions migrate to the B site and an equal amount of Fe^{3+} ions migrate to the A site resulting in J_{AB} interaction. These distinctive properties of nano-zinc ferrite have been ascribed to surface effects or surface magnetism [3]. Authors of this article had carried out a systematic study on nanosized zinc ferrite and established that Zn^{2+} ions occupy B sites instead of A sites and are found to exhibit ferrimagnetic behavior at reduced dimensions [4,5]. Low Energy Ion Scattering (LEIS) studies on spinel structures revealed that it is the octahedral sites that are preferentially exposed on the surface [6]. Anantharaman *et al.* carried out LEIS studies on ultrafine zinc ferrite and observed that the amount of zinc on the surface increases with decrease in particle size [5]. This is a clear indication of cation redistribution in the nano-regime and it was observed that the distribution is synthesis specific [7–9]. Such disordered spinels can be represented by $[Zn_{1-x}{}^{2+}Fe_x{}^{3+}]_A[Zn_x{}^{2+}Fe_{2-x}{}^{3+}]_BO_4$, where x represents the degree of cation disorder/percolation depth.

The thin film form of zinc ferrite can be easily integrated into devices which find application as various gas sensors. Hence thin film forms of these materials assume importance from an application point of view. From a fundamental perspective thin films of zinc ferrite have attracted researchers due to their anomalous magnetic behavior. The dependence of preparation method, effect of thickness and the influence of annealing on various properties of zinc ferrite thin films are of great interest to scientific community.

Among the various methods used for preparing zinc ferrite thin films, namely, sputtering, Pulsed Laser Deposition and spin coating, sputtering stands out among other techniques. It is presumed

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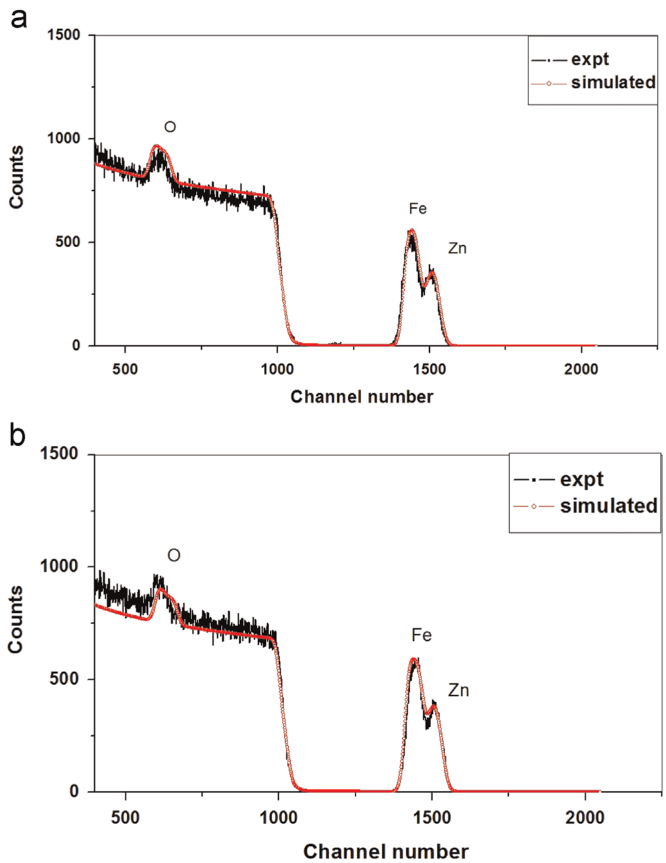

Fig. 1. RBS spectrum of (a) pristine film and (b) film annealed at 600° C.

that when zinc ferrite thin films are prepared by RF sputtering, the high energy imparted to the zinc ferrite results in random arrangement of Fe and Zn ions in the A and B sites. This random distribution of cations gives rise to interesting magnetic properties like superparamagnetism, glassy behavior or ferrimagnetic properties in zinc ferrite thin films.

Existing school of thoughts on the unusual magnetic behavior of zinc ferrite in the nanoregime do not provide a conclusive answer. Studies on zinc ferrites are still a hot topic of research due to the varied and incoherent results obtained by different groups [10–16]. For example, Nakashima *et al.* prepared zinc ferrite thin films by RF sputtering and they observed coexistence of ferrimagnetic ordering and glassy behavior [9]. Bohra *et al.* carried out systematic studies on zinc ferrite thin films prepared by RF sputtering and Pulsed Laser Deposition and they obtained high magnetisation but the film did not saturate even at the highest applied field [17]. Yamamoto *et al.* realized room temperature cluster glass state in zinc ferrite thin films prepared by Pulsed Laser Deposition (PLD). They investigated the role of deposition rate on the magnetic properties of these thin films. The room temperature spin glass property has been found useful in making magneto optic memory devices [7]. Recently Liang *et al.* reported deposition of zinc ferrite thin films on various substrates. They obtained a saturation magnetisation of 1.5×10^{-3} emu/cc for a 120 nm thick film [18] which is very small for any useful application.

It is in this context that a thorough investigation on zinc ferrite thin films assumes importance. Thermal annealing of thin films of zinc ferrite can result in alteration of surface characteristics leading to modified magnetic and structural properties. Moreover the effect of annealing on the cation redistribution, if any, can also be investigated. In the present study zinc ferrite thin films were prepared by employing RF sputtering. The films were annealed at 400° C and 600° C. The structural and magnetic properties of zinc ferrite thin films and the effect of thermal annealing on the magnetic properties are investigated.

2. Experimental methods

Zinc ferrite thin films were coated on silicon substrate by RF sputtering from a phase pure zinc ferrite target. The phase pure target employed for sputtering was in turn prepared by sol–gel auto combustion technique using zinc nitrate and ferric nitrate in the ratio of 1:2 as precursors. This was dissolved in ethylene glycol by adding a solvent under constant stirring at 70° C and the obtained sol was heated at 120° C until auto combustion took place. The powder thus obtained was pressed into pellets of 5 cm diameter and then annealed at 700° C for 24 h. The sputtering was carried out in an Argon atmosphere with an RF power of 150 W for 90 min. Vacuum of 5×10^{-5} Torr was attained with the help of a turbo pump backed by a scroll pump and during deposition the pressure increased to 2×10^{-2} Torr. The films obtained were annealed at 400° C and 600° C for 1 h in air. Rutherford Backscattering Spectrometry (RBS) was employed to determine the thickness and composition of films. Measurements were performed at Pelletron Accelerator RBS-AMS Facility (PARAS) at Inter University Accelerator Centre (IUAC), New Delhi. The experimental results are fitted using XRUMP (RBS Analysis and Simulation package) software to obtain thickness and composition [19]. Structural characterization of films were carried out using Glancing X-Ray Diffractometer (GXRD) Bruker Discover D-8 with Cu Kα ($\lambda = 1.5406$ Å) radiation at a glancing angle of 1°. The crystallite size was calculated using Scherrer formula, $D = \frac{0.9\lambda}{\beta \cos\theta}$ where D is the crystallite size, λ wavelength of X rays, β full width at half-maximum in radians and 2θ the diffraction angle. Micro-structural characterization was carried out using Transmission Electron Microscope (TEM) and Selected Area Electron Diffraction (SAED). Nanoscope IIIa Digital Instruments, Veeco was employed for surface morphology studies and the analysis of AFM images was done using the offline AFM software. Room temperature and low temperature magnetic measurements were conducted employing a 7 T MPMS SQUID–VSM. *MH* loops at room temperature and at 10 K was traced. Field cooled–Zero field cooled (FC–ZFC) measurements were carried out at a cooling field of 100 Oe and 1000 Oe.

3. Results and discussions

The thickness of the pristine film estimated using RBS data was around 120 nm. The weight percentage of elements was found to be 12.5% ± 4% Zn, 25% ± 1.3% Fe, 62.5% ± 1.1% O. A ratio of 1:2 of Zn:Fe was achieved in thin films, which is identical to the target composition. The thickness and composition of films do not vary on annealing which suggests that the films are uniform. RBS spectra for pristine and annealed films are depicted in Fig. 1.

The GXRD pattern is shown in Fig. 2. The pristine film exhibits a broad peak at 35°; on annealing at 600° C, the peak corresponding to (311) plane became prominent and the crystallite size calculated using Debye–Scherrer formula was 18.2 nm. To support the results from GXRD, SAED measurements were performed and are shown in Fig. 3a and b. The *d* values were compared with the standard *d* values of zinc ferrite and are in good agreement. The (311) planes are clearly visible in the SAED pattern of pristine film, which could not be detected in the case of GXRD [20]. The particle size calculated from TEM is 12 ± 1.3 nm and 16 ± 1.9 nm respectively for pristine and film annealed at 600° C (Fig. 3c–f). Thus we observe that zinc ferrite films are crystalline in nature and the grains grew