Materials Research Bulletin 61 (2015) 475–480

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Microstructure and magnetic properties of patterned nano crystalline zinc ferrite thin film fabricated by pulse laser deposition

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ARTICLE INFO

Article history:
Received 12 June 2014
Received in revised form 17 October 2014
Accepted 27 October 2014
Available online 29 October 2014

Keywords:
Thin films
Laser deposition
Microstructure
Magnetic properties

ABSTRACT

Patterned nano crystalline $ZnFe_2O_4$ thin film was fabricated on quartz substrate by pulse laser deposition. XRD and Raman spectroscopic techniques were employed for structural characterization of the film. Silencing of a small number of prominent ferrite XRD peaks in thin film signify mild textured film growth. The observed XRD peak position swing with respect to the target material in thin film indicates formation of lateral strain in opposite directions during film growth. The thin film XRD peak position shift with target material data as reference is explained by suggesting an appropriate film growth model. Designated ferrite Raman emission peaks originated from film surface authenticates the stoichiometric and structural stability of ferrite material. AFM images indicate specific pattern formation with nanogranular morphology. Magnetic property measurements of the thin film revealed enhanced properties which are explained on the basis of texture, lattice strain, and surface features that are originated from patterned thin film growth.

1. Introduction

The Interest in ferrite thin films is derived from their potential applications in high-frequency electronics and information storage devices [1,2]. The physical properties of ferrites in thin film form may vary with respect to its bulk counterpart. Although properties of nano ferrites are fairly well understood in powder form, deposition factors do affect the microstructure of the film, which in turn characterize the properties of the material in thin film [3]. Most reported results showed an increase in coercivity and decrease in magnetization due to the nanocrystalline nature of the material in films [4]. Bulk zinc ferrite, having normal spinel structure and exhibit paramagnetic properties, show magnetic order in its nanoparticles at room temperature [5–7]. Similar observations of magnetization are reported in Zn ferrite thin films [8–11]. Nanocrystalline zinc ferrite material which had already gained interest due to its unique magnetic properties that differ substantially from its bulk counterpart find industrial applications in electronic component manufacture as a common ingredient for technologically important Ni–Zn and Mn–Zn mixed ferrites [12,13]. The miniaturization of electronic components compels the industry to seek favorable thin film magnetic properties for possible device fabrications.

Any ferrite thin film growth process on amorphous substrates find instant industrial applications if compatible with integrated circuit technology. In process applications wherein magnetic oxides are to be integrated on to semiconducting materials, low processing temperature is a preferred prerequisite to avoid possible chemical reaction with metal atoms present in device structures. In comparison with other techniques, pulse laser deposition (PLD) provides increased atom mobility during film deposition owing to high kinetic energy of the vaporized material in laser plume. This helps in formation of homogeneous film microstructure, without any distortion of target stoichiometry. Further this technique may possibly lower the substrate processing temperature required for crystallization.

To a certain extend magnetic properties of thin films are shaped on the basis of the microstructure evolved during film growth. Some growth parameters that affect the microstructure of the film are substrate temperature, thermal expansion coefficient, lattice

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http://dx.doi.org/10.1016/j.materresbull.2014.10.061
0025-5408/

mismatch between the film and substrate, deposition time, and target-substrate distance. Film surface effects can also lead to strong deviations in properties, which additionally depend on film thickness. There is also a possibility of micro structure deviation at interface layers leading to variation in properties of the films.

Based on the preparative conditions one can obtain a wide variety of different surface morphologies and film microstructures [14]. In an occurrence of non epitaxial film growth in layer-by-layer mode, the growth front can be rough in the form of mounds. Supplementary to it, noise induced roughening during the growth can guide to the formation of self-affine fractal morphologies [15]. Another factor that robustly alters the growth characteristics is the kinetic effect stress relaxation occurring in film interfaces. These essentially related to dynamic growth mechanism, have a significant and generally diverse influence on physical properties of the material in thin film format [16,17]. All above referred and reported physical phenomena motivated us to view the deposition of patterned zinc ferrite thin film as an interesting feature for investigation and study its magnetic properties.

2. Experimental

Nanoparticle $ZnFe_2O_4$ ferrite material was prepared in our laboratory by precipitating aqueous solutions of $ZnSO_4$ and $FeCl_3$ mixtures in alkaline medium. The powdered sample was palletized at 15 ton pressure and sintered at 450 °C temperature for 4 h in normal atmosphere and used it as target material for thin film preparation by laser ablation. The laser ablation was carried out on a quartz substrate at a chamber pressure of 2×10^{-6} T using Excimer laser KrF (248 nm) (Lambda Physik COMPex 201 model). The laser energy was maintained at 220 mJ with a repetition rate of 10 Hz. The deposition was performed for 30 min on the substrate maintained at an elevated temperature of 450 °C. The optimized target to substrate distance was 4.5 cm. The focused laser beam was incident on the target surface at an angle of 45° with the target spin fixed at 10 rpm. After deposition, the thin film was cooled down to room temperature at the rate of 5 °C/min, maintaining the pressure in the vacuum chamber at 2×10^{-6} T. The prepared thin film was characterized on Bruker AXE D8 X-ray diffractometer with Cu Kα radiation at room temperature in standard $\theta/2\theta$ mode. The thickness measurement of the film was carried out on AMBIOS XP-1 stylus profiler with 0.5 nm resolution. Raman spectra of the thin film sample was taken on HORIBA Jobin Yvon LabRAM HR 800 Micro Raman spectrometer with argon ion laser source having wavelength 514 nm in a spectral resolution of 1 cm^{-1}. The AFM image of the film taken on SPM (Digital Nano-Scope-III) in contact mode was used for surface analysis of the film and particle size determination. Magnetic measurements of the target material in powder form were carried out on Quantum Design 3-tesla VSM (VersaLab). The thin film magnetic data is generated on Quantum Design's MPMS SQUID VSM.

3. Results and discussion

The X-ray diffraction pattern (XRD) of $ZnFe_2O_4$ target material and deposited thin film is shown in Fig. 1.

The target material XRD data reveal peak positions which are in agreement with reported values of JCPDS files (JCPDS card No. 74-2397) which confirm single phase cubic spinel structure of the sample [18]. From XRD data the interplanar spacing (d) is calculated using Bragg's law and the average lattice parameter (a = 8.47) is obtained using "Eq. (1)".

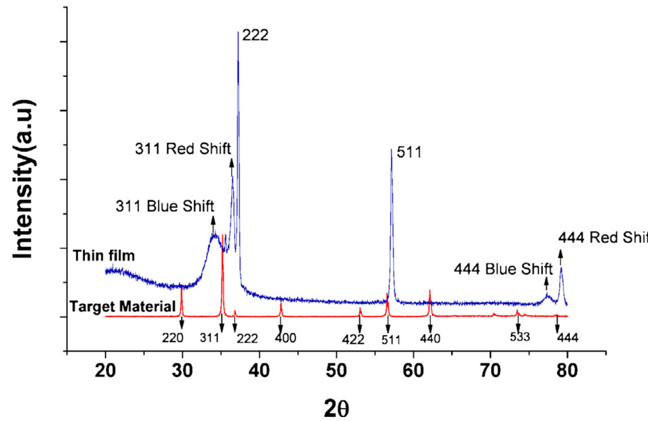

Fig. 1. XRD pattern of $ZnFe_2O_4$ target material and thin film.

$$\frac{1}{d_{hkl}} = \frac{\sqrt{h^2 + k^2 + l^2}}{a} \quad (1)$$

The particle size of the sample (44 nm) was obtained by performing peak broadening measurements (FWHM) for each peak, substitution in Debye–Scherrer equation (Eq. (2)) and averaging over all seven major peaks.

$$D = \frac{0.9\lambda}{\beta \mathrm{Cos}\theta} \quad (2)$$

The thin film XRD pattern does not contain all the designated ferrite spinel peaks. Non appearance of certain prominent ferrite peaks and enhancement of peak intensities in some preferred crystallographic orientations which were otherwise feeble in the XRD pattern of the target material is a convincing signature of textured thin film growth. In PLD process the ablation temperature is lower than the melting temperature of target, the film growth is far from equilibrium and the ablated atoms do not have enough mobility to achieve the lowest thermal dynamic energy state. Since the film was deposited at optimized temperature and deposition rate, a large strain could be induced in the interface between the ferrite film and quartz substrate during the initial phase of film growth. Further, the difference of thermal coefficient between the film and substrate may well induce strain/stress during film growth [19]. Thus, the formation of texture could be attributed to the minimization of strain energy density.

It is worth noting the observed XRD peak shifts in ferrite thin film sample. There is an appreciable shift in peak position (blue shift) in respect of intensity peak representing 3 1 1 crystal planes. This peak shift arising out of shift towards large inter-reticular distance can be explained with the help of atomic peening phenomena [20]. The deposition of the target species on to the substrate using PLD involves disintegration of the species from target by high energy pulsed laser, transportation of it through the laser plume and deposition on to the substrate preceded by a bombardment. A bombardment on substrate layer by energetic species generates a compressive stress in crystal planes parallel to the film surface, which in turn generates an expansion in the planes normal to the surface. This stress and the corresponding strain results in an increase of the lattice parameter (8.4 Å–8.7 Å) normal to the surface, which explains the blue shift observed in the X-ray diffraction pattern [21,22].