Materials Science-Poland, 31(4), 2013, pp. 581-586
http://www.materialsscience.pwr.wroc.pl/
DOI: 10.2478/s13536-013-0142-4

Effect of low oxygen pressure on structural and magnetic properties of quenched $SrFe_{12}O_{19}$ thin films

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Strontium hexaferrite thin films have been grown on glass substrates at room temperature in oxygen environment by pulsed laser deposition method. The effect of oxygen pressure (p_{O2}) on the structural and magnetic properties has been investigated. The as-deposited films were found to be amorphous in nature. The crystallization of these films was achieved by annealing at a temperature of 850 °C in air. The thickness of the film increased with p_{O2}. The film grown at $p_{O2} = 0.455$ Pa had a clear hexagonal structure. The values of coercivity for the films were found to increase with p_{O2}.

Keywords: *thin films; pulsed laser deposition; hexaferrites; magnetic properties*

1. Introduction

Hexagonal ferrites such as $SrFe_{12}O_{19}$ and $BaFe_{12}O_{19}$ have been used for high density recording and millimetre wave applications [1]. Strontium hexaferrite (SrM) films are an attractive material for high density magnetic recording because of high anisotropy field, mechanical hardness and good chemical stability. For high density recording applications, polycrystalline films with small grain sizes and magnetic easy axis oriented either normal or parallel to the film plane are appropriate [2].

The crystallographically oriented films have been deposited by various methods [3–5]. Among different successful techniques, laser ablation appears to be one of the most promising because of its ability to control film thickness and composition during deposition.

The crystallographic and magnetic properties of pulsed laser deposited (PLD) SrM thin films were improved by using appropriate substrates such as (0 0 0 1) sapphire [6], (0 0 1) sapphire [2], (1 1 0) sapphire [7], $Gd_3Ga_5O_{12}$ [7] and silicon wafer [7] with in-situ [2, 6] and post deposition [2, 6] annealing methods. Those films were either deposited at high oxygen pressures along with high temperature post or pre- annealing or on different costly substrates. Recently there have been few reports on fast annealing or quenching [7–9] of SrM thin films for the enhancement of the texture, c-axis oriented grains in the films.

In the present investigation, for the first time, a good crystalline c-axis oriented strontium hexaferrite (SrM) thin films have been deposited on glass substrates using PLD at the oxygen pressure (p_{O2}) range of 0.02 Pa to 0.455 Pa. The as-deposited thin films were annealed at 850 °C in an open furnace and cooled down to room temperature. The effect of p_{O2} on structural and magnetic properties of quenched thin films was studied and discussed in the present paper.

2. Experimental

In the present investigation, the thin films were grown on glass substrates by using PLD method.

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The target of $SrFe_{12}O_{19}$ was prepared by solid state method using strontium carbonate ($SrCO_3$) and ferric oxide (Fe_2O_3). The powders were calcined at 900 °C/8h. The calcined powders were mixed with appropriate amount of binder and pressed into 1 inch diameter pellet. The green pellet was sintered at 1200 °C/6h using a conventional sintering method to obtain the target for laser ablation. The strontium hexaferrite thin films were grown on ordinary glass of 1mm thickness by PLD method.

As a light source, a Lambda Physik ComPex excimer laser ($\lambda = 248$ nm) with 10 Hz repetition rate was used to ablate the target. The laser beam was focused on the rotating target at an incidence angle of 45° against the normal to surface. The laser was focused onto the target to give a fluency of about 5 J/cm^2. The target and the substrate were mounted in a vacuum chamber which was pumped down to a base pressure of 2.6×10^{-5} Pa before the introduction of oxygen gas. The distance from the target to the substrate was 4 cm. The deposition time for all the films was 80 min. The target rotated during the laser ablation in order to avoid texturing of its surface.

The deposition of SrM films was carried out at different p_{O2} in the range of 0.02 Pa to 0.455 Pa without any post annealing. All the films at room temperature were found to be amorphous in nature. The crystallization of amorphous films was achieved by annealing at a temperature of 850 °C in air and the films were slowly cooled down to room temperature. This method is a new technique to prepare a well crystallized and smooth film.

The effect of p_{O2} on the phase and morphology of the examined thin films was studied using XRD. The topographical images were recorded using an atomic force microscope (AFM) operating in non-contact mode. The recorded AFM images were used to determine the roughness and grain size of the films. The thickness of the films was measured using a surface stylus profilometer (Ambios tech model XP-1). The room temperature saturation magnetization (M_s) and coercive field (H_c) were studied using vibrating sample magnetometer (VSM) up to 15 kOe.

3. Results and discussion

Fig. 1(a) shows the XRD pattern of SrM target sintered at 1200 °C/6h. All diffraction peaks of the target are indexed and matched well with the JCPDS No: 80-1197. The lattice parameters of the target were found to be a = 5.892 Å and c = 23.054 Å. Similar results were reported by other researchers and the lattice constants were comparable with them [10]. The films were deposited under different oxygen pressures keeping all deposition parameters unchanged. Fig. 1(b – e) shows the films deposited under different oxygen pressures and annealed at 850 °C. The films deposited at a pressure less than $p_{O2} = 0.02$ Pa and annealed below 850 °C were amorphous in nature. The influence of oxygen pressure on the film structure was more important than the influence of substrate temperature. A clear crystallographic c-axis orientation of (0 0 6), (0 0 8) and (0 0 14) with random orientation of the grains along (1 0 7), (1 1 4), (2 0 11) could be observed in the film deposited at $p_{O2} = 0.455$ Pa. In fast annealed films when the oxygen pressure increased, the texture of the film changed from (0 0 1) orientation to random orientation. The lattice parameters of the film deposited at $p_{O2} = 0.455$ Pa were found to be a = 5.876 Å and c = 23.235 Å. The broad diffraction peak in the range of $30° \leqslant 2\theta \leqslant 40°$ was due to the hexaferrite phase along with secondary phases which produced strain and defects in the film, as seen in Fig. 1d. When the p_{O2} increased from 0.02 Pa to 0.455 Pa, the secondary phases converted into hexaferrite phase and at higher oxygen pressure hexaferrite formation was complete. It is also observed that the intensity of the peaks has increased which implies the increase in crystallite size. The effective strain in the film is given by $\frac{\Delta d}{d}$, where $\Delta d = d - d_o$, d and d_o are the lattice spacing of a bulk sample and a film respectively. The effective strain of the film at $p_{O2} = 0.455$ Pa is 27 %.

P. Papakonstantinou et al. have reported that the film deposited on sapphire substrate above and below 10 Pa p_{O2} and annealed at 840 °C showed good c-axis perpendicular orientation of crystallites [2]. T.Y. Hylton et al., showed that a good quality crys-

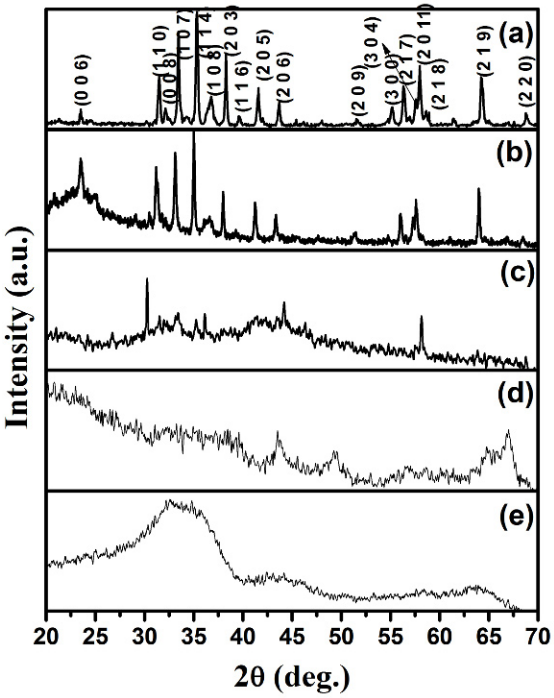

Fig. 1. XRD patterns of (a) SrM target and the SrM films deposited under different pressures: (b) 0.455 Pa (c) 0.202 Pa (d) 0.05 Pa (e) 0.02 Pa.

talline thin films were achieved through post deposition annealing in an oxygen atmosphere at relatively high temperature above 800 °C [11]. Our films showed good crystallinity at low oxygen pressures compared to above methods.

The orientation of grains in the films can be evaluated using a function R, which gives a measure of average c-axis orientation with respect to the film plane and is given by:

$$R = N \sum_i \cos\theta_i \left(\frac{I_i}{I_{oi}}\right) \tag{1}$$

and

$$N = 1 \left[\sum_i \left(\frac{I_i}{I_{oi}}\right)\right]^{-1} \tag{2}$$

where θ_i is an angle between c-axis of a particular crystallite and the normal to the film plane, I_i are the intensities of x-ray diffraction lines of the film and I_{oi} are the corresponding powder diffraction pattern intensities. The value of R function is 1 for a pure perpendicular texture (*0 0 l*), zero for (*h k 0*) and 0.5 for random c-axis orientation. The R value for the film obtained at $p_{O2} = 0.455$ Pa is 0.465. It is clear from the XRD peaks and R value that the grains are randomly oriented along c-axis. These orientations may be due to the fact that when the thermal energy increases, the atom mobility allows a more effective rearrangement and consequently, a preferential orientation of the film is possible [9]. It is found from the XRD patterns that the c-axis orientation of the crystallites is strongly dependent on p_{O2}.

Fig. 2(a – d) shows the AFM images of the SrM thin films deposited at different p_{O2}. It is clearly seen that with an increase of p_{O2} the grains morphologies are changed from circular shape to elongated shape. The spherical grains represent the alignment of basal plane parallel to the sample plane (c-axis perpendicular), while the elongated grains provide basal plane perpendicular (c-axis in-plane) to the sample plane [12]. The same results were also observed for barium hexaferrite films deposited on sapphire substrate at $p_{O2} = 33.33$ Pa and post annealed at 900 °C [13]. In Fig. 2c the elongated grains may exist due to the presence of some screw dislocation components. The addition of few atoms to the substrate before the film deposition produces defects and strain in the film. These defects with screw components can act as preferential nucleation sites leading to the growth of the ferrite grains during deposition. This growth mechanism increases the dislocation density by adding atoms to the spiral steps of screw dislocations, which can be seen in Fig. 3d. Therefore, by increasing oxygen pressure the atom mobility and surface diffusion of atoms to the growth steps increases. The enhanced growth of the grains with p_{O2} results in the increase of the thickness of the film and formation of hexaferrite phase which is evident from Fig. 1c.

The AFM images were used to evaluate the grain size, surface morphology and magnetic structure of the films. The AFM images of the SrM films with different thicknesses are shown in Fig. 2. The grains in the films have good crystallinity with hexagonal shape. This indicates that the films have grown with c-axis normal to the film plane, which is consistent with the XRD results. The average

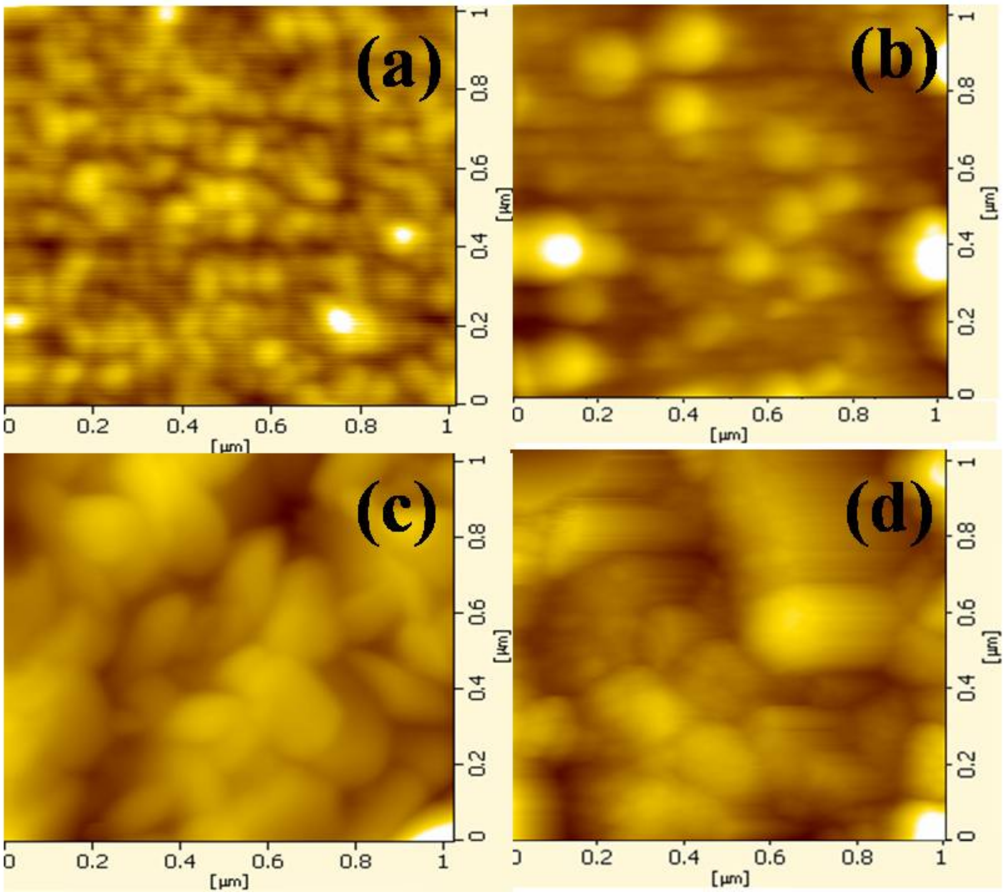

Fig. 2. AFM images of thin films deposited at (a) 0.02 Pa (b) 0.05 Pa (c) 0.202 Pa (d) 0.455 Pa.

grain size measured by the linear intercept method increased in the range of 100 – 250 nm with the film thickness due to in-situ heating effect during its deposition. Root mean square (RMS) is a term used to measure statistically the roughness of a surface. The RMS surface roughness of the films increased in the range of 9 to 24 nm with an increase of p_{O2}.This is due to variation in the distribution of incident angles and energy of deposited atoms at low and high oxygen pressure [14]. The surface roughness does not significantly affect the magnetic properties of present thin films but the demagnetizing factor is affected. The surface roughness of the films is influenced by p_{O2}. The values of RMS are given in Table 1.

Fig. 3 shows the magnetization curves of SrM thin films deposited under different p_{O2} and annealed at 850 °C. It is clearly seen that the shape of the curves depends on p_{O2} and the films are magnetically aligned with an increase of p_{O2}. The available field is not sufficient to saturate the films. The shapes of the loops in Figs. 3c and 3d are found to be similar to the magnetization loops of $SrFe_{12}O_{19}$ grown by electron beam deposition on Al_2O_3 annealed at 700 °C and 900 °C, respectively [4]. The

Table 1. Data of grain size, RMS, thickness and coercive field of SrM thin films.

p_{O2} (Pa)	Grain Size (nm)	RMS (nm)	Thickness (nm)	H_c (Oe)
0.02	80	9	477	394
0.05	110	12	709	462
0.20	190	17	729	496
0.45	280	24	1065	545

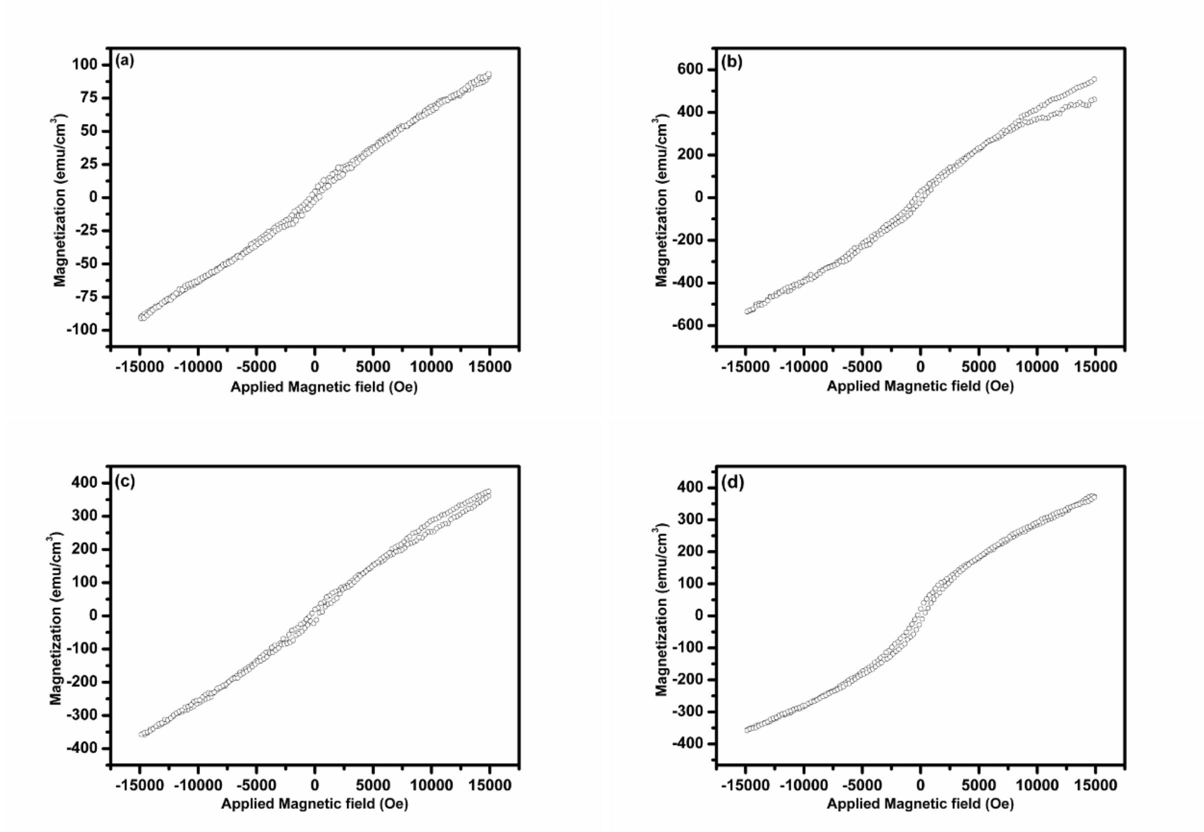

Fig. 3. Magnetization curves of strontium ferrite thin films deposited at (a) 0.02 Pa (b) 0.05 Pa (c) 0202 Pa (d) 0.455 Pa.

coercive field (H_c) values are given in Table 1. It is clearly seen that the coercive field values increase with p_{O2} which suggests that the average c-axis orientation is tilted from the film normal. The high value of H_c is attributed to the domain wall pinning which results from the defects. But the values are much more less than the bulk values of $SrFe_{12}O_{19}$ [15]. The magnetic properties are dependent on film thickness.

4. Conclusions

The SrM thin films were grown on glass substrate by PLD method. The films deposited at oxygen pressures of 1 Pa and at substrate temperatures of 850 °C were fully dense and showed good crystallinity, morphology and magnetic properties. In fast annealed films when p_{O2} increases, the texture of the film changes from (0 0 1) orientation to random orientation. The high value of H_c is due to the presence of defects.

Acknowledgements

The authors are thankful to University Grants Commission (UGC), New Delhi for providing financial assistance through Dr D.S. Kothari Postdoctoral fellowship to carry out the present research work.

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Received 2013-01-25
Accepted 2013-10-06