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Effect of annealing time on structural and magnetic properties of laser ablated oriented Fe_3O_4 thin films deposited on Si(100)

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Abstract. **We have fabricated ∼143 nm Fe_3O_4 thin films on Si(100) substrates at 450°C and then annealed them at the same temperature for 30, 60 and 90 min under a vacuum of 10^{-6} torr with pulsed laser deposition. We studied the effects on the structural and magnetic properties of Fe_3O_4 thin films. The films have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and vibrating sample magnetometry (VSM). XRD studies showed pure single phase spinel cubic structure of Fe_3O_4 with a preferential [111] orientation, independent of substrate orientation at 90 min annealing. Higher magnetization was obtained up to 60 min annealing due to Fe phase but at 90 min, we obtained reduced magnetization of 335 emu/cc. This is attributed to the formation of antiphase boundaries between substrate and film.**

Keywords. **Iron oxide; Fe_3O_4 thin film; pulse laser deposition; annealing; saturation magnetization.**

1. Introduction

Fe_3O_4 is a promising half metallic ferrimagnetic material and has the ability to inject 100% spin polarized electrons (Versluijs *et al* 2001; Wolf *et al* 2001). As compared to other half metallic materials such as NiMnSb, CrO_2, $La_{0\cdot7}Sr_{0\cdot3}MnO_3$ (Sensor *et al* 1999; Coey and Venkatesan 2002), Fe_3O_4 has a higher Curie temperature of 850 K (Brabers 1995) which makes it a strong candidate for spintronic devices (Fabian and Das Sarma 2004).

Due to their technological importance, numerous studies are reported of depositing highly oriented epitaxial or polycrystalline Fe_3O_4 films techniques such as molecular beam epitaxy (MBE) (Voogt *et al* 1998; Ferhat and Yoh 2007), electron beam ablation (Dediu *et al* 2007), reactive sputtering (Magulies *et al* 1996; Liu *et al* 2003; Park *et al* 2003) and pulsed laser deposition (PLD) (Gong *et al* 1997; Parames *et al* 2006). It is well known that in addition to the desired Fe_3O_4 phase, several other phases can co-exist such as Fe_3O_4, FeO and Fe according to specific deposition conditions (Lochner *et al* 1994; Voogt *et al* 1999; Park *et al* 2003). However, it is still difficult to grow them with well defined compositions with PLD from different targets.

A few reports about the effects of temperature on the structural and magnetic properties of Fe_3O_4 thin films also exist. In the present work, we study the effect of annealing time on the structural and magnetic properties of Fe_3O_4 thin films on Si(100) substrates deposited from PLD. Phase analysis of the films was carried out by X-ray diffraction with CuKα radiation. Grain size, lattice strain and lattice constants were measured by the Williamson–Hall plot (Voogt *et al* 1999), assuming that the peak shapes are Lorentzian. Crystal structure determination was performed using the PowderX software (Williamson and Hall 1953). Film thickness and magnetic properties were determined from scanning electron microscopy (SEM) and vibrating sample magnetometery (VSM), respectively.

2. Experimental

Fe_3O_4 thin films were grown on Si(100) substrates by pulsed laser deposition (PLD) from Fe_3O_4 target. Before deposition the substrates were cleaned with isopropanol in an ultrasonic bath for 20 min and then annealed at 500°C for 30 min under a vacuum of 10^{-7} torr. A Nd:YAG laser (EKSPLA) of wavelength, 248 nm and pulse duration, 3–6 nm, was used to ablate the target. The target was rotated at the rate of 10 rpm to avoid any crack formation on the target. The pulse repetition rate was adjusted at 10 Hz and the energy density of the laser beam at the target was 1·3 J/cm^2. Deposition was carried out at a substrate temperature of 450°C for 20 min under a working pressure of 10^{-6} torr after

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adjusting the flow rate of oxygen to 0·3 sccm while the target to substrate distance was held fixed at 36 mm. We annealed the films for 30, 60 and 90 min at the same temperature under a vacuum of 10^{-7} torr and after stopping the flow of oxygen. After deposition and annealing were complete, the substrates were cooled at 5°C/min. The film thickness, crystal structure and magnetic properties were determined by cross-sectional scanning electron microscopy (SEM), X-ray diffractometry (XRD) and vibrating sample magnetometry (VSM), respectively.

3. Results and discussion

Figure 1 shows X-ray diffraction patterns of Fe_3O_4 thin films on Si(100) substrates suggesting that all the films are grown with preferred orientation in the [111] direction except the cubic structure. An additional iron phase appears at ≈45° up to 60 min annealing, but at 90 min annealing, pure single phase Fe_3O_4 is obtained. We have calculated the lattice parameters using PowderX (Dong 1999). These are slightly less than the bulk material and are presented in table 1. This is due to substrate induced strain in the film.

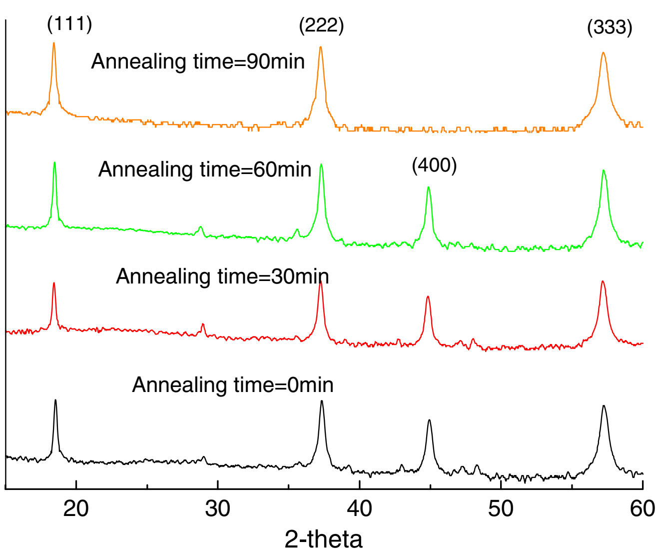

Figure 1. XRD pattens of films annealed for 0, 30, 60 and 90 min.

Table 1. XRD and VSM analyses of annealed Fe_3O_4 thin films on Si(100) substrates.

Annealing time (min)	Lattice constants (Å)	Grain size (nm)	Lattice strain	Saturation magnetization (emu/cc)	Coercivity, H_c (Oe)
0·0	8·378	157	0·0084	402·85	303
0·30	8·377	127	0·0075	420·00	306
0·60	8·367	120	0·0068	640·00	272
0·90	8·366	18	0·0010	335·00	315

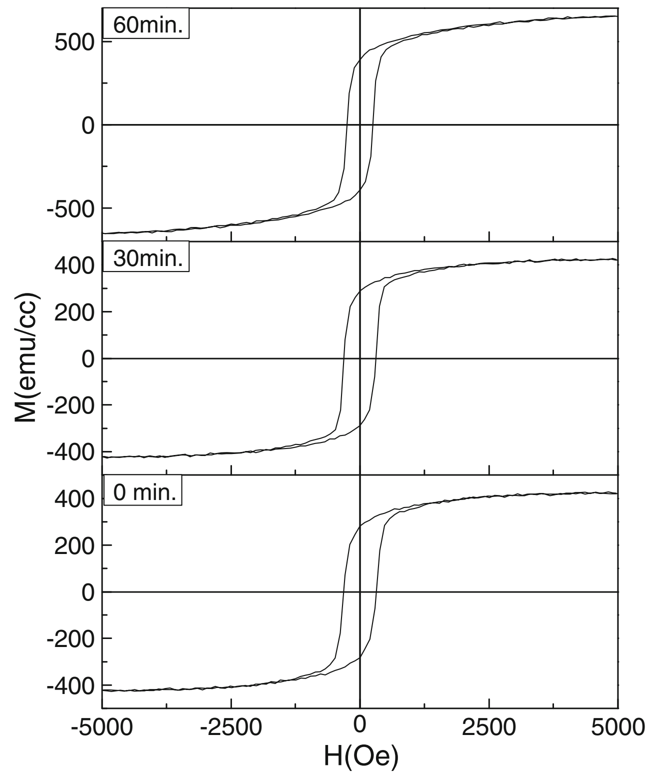

Figure 2. Room temperature M–H loops of film annealed for 0, 30 and 60 min.

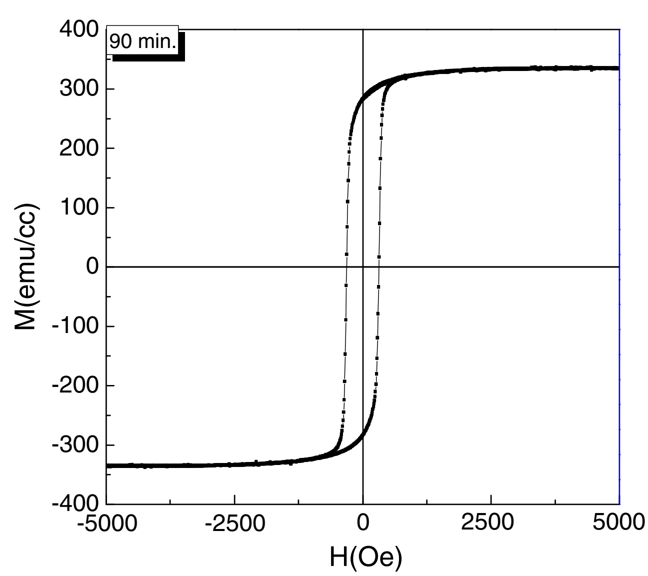

Figure 3. Room temperature M–H loop of film annealed for 90 min.

The most interesting point is that at 90 min annealing, we got pure preferential growth of the film in [111] direction. As reported by Tiwari *et al* (2007a), this may be due to the large lattice mismatch between the films and substrates. As the substrate control over the film growth is weak, the preferred orientation is determined by the thermodynamically stable state having a minimum internal energy (Tiwari *et al* 2007b).

Figures 2 and 3 show room temperature magnetization hysteresis behaviour for all the films. We obtained a low saturation magnetization in all the films as compared to bulk material, except the film that is annealed at 60 min. This lowering of saturation magnetization may be due to the presence of antiphase boundaries between the films and substrates (Magulies *et al* 1996). Similar results have also been reported earlier by Tiwari *et al* (2007a).

4. Conclusions

In conclusion, Fe_3O_4 thin films were deposited with pulsed laser deposition technique on Si(100) substrates at 450°C for 30, 60 and 90 min annealing times. XRD patterns of the films imply the single phase spinel cubic structure with [111] orientation at 90 min annealing. It was found that the grain size and lattice strain decreased with increase in annealing time. Magnetization results showed ferromagnetic behaviour for all the films, with saturation magnetization lower than the bulk material which may due to the presence of antiphase boundaries between films and substrates.

References

Brabers V A M 1995 *Handbook of magnetic materials* (ed) K H J Buschow (Amsterdam: Elsevier Science) **Vol. 8**

Coey J M D and Venkatesan M 2002 *J. Appl. Phys.* **91** 8345

Dediu V, Arisi E, Bergenti I, Riminucci A, Solzi M, Pernechele C and Natali M 2007 *J. Magn. Magn. Mater.* **316** e721

Dong C 1999 *J. Appl. Cryst.* **32** 838

Fabian Z J and Das Sarma S 2004 *Rev. Mod. Phys.* **76** 323

Ferhat M and Yoh K 2007 *Appl. Phys. Lett.* **90** 112501

Gong G Z, Gupta A, Xiao G, Qian W and Draivid V P 1997 *Phys. Rev.* **B56** 5096

Liu H, Jiang E Y, Bai H L, Zheng R K, Wei H L and Zhang X X 2003 *Appl. Phys. Lett.* **83** 3531

Lochner E, Shaw K A, DiBari R C, Portwine W, Stoyanov P, Berry S D and Lind D M 1994 *IEEE Trans. Magn.* **30**

Magulies D T, Parker F T, Spada F E, Goldman R S, Li J, Sinclair R and Berkowitz A E 1996 *Phys. Rev.* **B53** 9175

Parames M L, Mariano J, Viskadourakis Z, Popovoco N, Rogalski M S, Giapintzakis J and Conde O 2006 *Appl. Surf. Sci.* **252** 4610

Park C, Shi Y, Peng Y, Barmak K, Zhu J-G, Laughlin D E and White R M 2003 *IEEE Trans. Magn.* **39** 2806

Sensor P, Fert A, Maurice J-L, Montaigne F, Petroff F and Vauress A 1999 *Appl. Phys. Lett.* **74** 4017

Tiwari S, Choudhary R J, Prakash R and Phase D M 2007a *J. Phys.: Condens. Matter* **19** 176002

Tiwari S, Prakash R, Choudhary R J and Phase D M 2007b *J. Phys.* **D40** 4943

Versluijs J J, Bari M A and Coey J M D 2001 *Phys. Rev. Lett.* **87** 026601

Voogt F C, Palstra T T M, Niesen L, Rogojanu O C, James M A and Hibma T 1998 *Phys. Rev.* **B57** R8107

Voogt F C, Fujii T, Smulders P J M, Niesen L, James M A and Hibma T 1999 *Phys. Rev.* **B60** 11193

Williamson G K and Hall W H 1953 *Acta Metall.* **1** 22

Wolf S A, Awschalom D D, Buhrman R A, Daughton J M, von Molnár S, Roukes M L, Chtchelkanova A Y and Treger D M 2001 *Science* **294** 1488