Growth and properties of pulsed laser deposited thin films of Fe_3O_4 on Si substrates of different orientation

Growth and properties of pulsed laser deposited thin films of Fe_3O_4 on Si substrates of different orientation

Shailja Tiwari, R J Choudhary, Ram Prakash and D M Phase[1]

UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore-452 017, India

E-mail: dmphase@csr.ernet.in

Abstract

Fe_3O_4 thin films were prepared by pulsed laser deposition on Si substrates of different orientations: (111), (100) and (110). X-ray diffraction studies revealed the spinel cubic structure of the films with preferential (111) orientation independent of the substrate orientation. Raman spectroscopy suggests the single-phase growth of Fe_3O_4 films on these substrates, with minimum full width at half maxima being observed for the film grown on Si(111) substrate. These samples exhibit room-temperature ferromagnetism, as observed by magnetization hysteresis. The magnetization in these films saturates at a magnetic field value of approximately 0.2 T.

1. Introduction

Magnetite (Fe_3O_4) is a well-known half-metallic ferromagnetic material and it enjoys the ability to inject 100% spin-polarized electrons [1, 2]. The Curie temperature of Fe_3O_4 is 858 K [3], which is very high compared to that of other half-metallic ferromagnetic materials. These properties make Fe_3O_4 a promising candidate for spintronic devices [4]. Magnetite has a cubic inverse spinel structure and it consists of Fe^{2+} and Fe^{3+} ions. These Fe ions occupy two different sites, tetrahedrally coordinated with four oxygen ions (site A), and octahedrally coordinated with six oxygen ions (site B). The A site is occupied by Fe^{3+} ions whereas Fe^{2+} and Fe^{3+} ions occupy B sites equally. Ions at B sites are aligned ferromagnetically but they are aligned antiferromagnetically with ions at A sites. Therefore, the magnetic moments of the Fe^{3+} ions are cancelled out and the net magnetic moment in Fe_3O_4 is due to Fe^{2+} ions, leading to the ferrimagnetic behaviour of magnetite. At room temperature the electrons continuously hop between Fe^{2+} and Fe^{3+} ions at B sites, leading to the metallic nature of the system. At 120 K, hopping is frozen and consequently the resistivity is increased by two orders of magnitude as the temperature is lowered. This transition is widely attributed to the transition

---

[1] Author to whom any correspondence should be addressed.

from a disordered phase to an ordered phase of Fe^{2+} and Fe^{3+} ions, which also brings in the structural transition from the cubic phase to the monoclinic phase. This transition is termed the Verwey transition [5].

Though the precise origin of the Verwey transition is still under review [6, 7], work is progressing in the direction of further harnessing the important features of magnetites for superior technological applications. In this milieu it is imperative to study the properties of Fe_3O_4 in thin-film form since for any application thin films finally hold the key. There are several reports available on thin-film growth of Fe_3O_4 by various techniques [8–10]. Most of these studies are on single-crystal MgO substrate, which possesses intrinsic growth defects of anti-phase boundaries (APBs) [9]. These defects lead to various unusual features, the most notable being the non-saturation of magnetization in thin films of Fe_3O_4. It turns out from these observations that the properties of magnetite are very sensitive to the extrinsic or intrinsic defects. In this context it is of worth to scrutinize the dependence of these properties on the silicon substrate. The significance of the Si substrate lies in the fact that most of the present-day technologies rely heavily on silicon. Therefore, the compatibility of Fe_3O_4 with Si will provide extra dimension to its applications.

There are a few reports on thin films of Fe_3O_4 on Si substrate [11–15]. Margulies *et al* [11] reported the growth of Fe_3O_4 films on Si(100) substrate by reactive sputtering technique and confirmed its stoichiometry by conversion electron Mossbauer spectroscopy. However, the film exhibited the Verwey transition at much lower temperature (at 104 K) as compared to the stoichiometric bulk sample. In another study, Tang *et al* [12] used the pulsed laser deposition technique to grow polycrystalline Fe_3O_4 on Si(001) substrate. They found that the Verwey transition temperature, T_V, for these films was 120 K; however, the films did not saturate magnetically even at a magnetic field as high as 2 T, and they attributed this to the presence of APBs in these nanocrystalline films. Similar observations were also presented by Tsai *et al* [13] in their work on DC sputtered polycrystalline films on Si(100) with a buffer layer of SiO_2. Jain *et al* [14, 15] in their work reported the growth of Fe_3O_4 on Si(001) substrate by an electron beam deposition technique, but either they required some buffer layer of Cu, Ta, Ti or SiO_2 to grow polycrystalline film or the films were amorphous in nature with two magnetic phases. Interestingly the electronic transport behaviour of these films highly depended on these buffer layers, which demonstrated variation in T_V from 65 to 155.5 K. They also observed a variation in their magnetic behaviour with the Cu buffer layer thickness. It is clear from these discussions that the properties of magnetite films highly rely on the deposition processes and conditions used. It is also noted that most of these studies are on Si(100)-oriented substrate, and the exploration of magnetite thin films on other orientations of silicon remained to be done. In the present paper we report our findings on pulsed laser deposited thin films of Fe_3O_4 on differently oriented single-crystal Si substrates: (100), (110) and (111). Here we show that our films are mostly oriented in the [111] direction irrespective of the orientation of the substrate used and without the requirement of any buffer layer, which further enhances the compatibility of magnetite with the existing Si technology. The films display a room-temperature magnetic hysteresis loop. To our best of knowledge, ours is the first successful attempt to grow oriented single-phase thin films of Fe_3O_4 on Si substrate.

2. Experimental details

Fe_3O_4 thin films were grown on Si(100), Si(110) and Si(111) substrates by pulsed laser deposition (PLD) from Fe_2O_3 target. The Fe_2O_3 target was prepared from Fe_2O_3 powder. The target was sintered at 900 °C for 8 h. A KrF excimer laser source ($\lambda = 248$ nm, pulse width $= 20$ ns) was used to ablate the target. During deposition the target was rotated at

Table 1. XRD analysis of Fe_3O_4 films on Si substrates.

Substrate	Particle size (nm)	Strain	Lattice constant (Å)
Si(100)	83	0.001 17	8.36
Si(110)	91	0.001 07	8.34
Si(111)	92	0.001 06	8.33

the rate of 10 rpm to avoid crater formation, which can direct the plume in some arbitrary direction and cause non-uniform deposition. The pulse repetition rate was set at 10 Hz and the energy density of the laser beam at the target was $2\,J\,cm^{-2}$. Deposition was carried out at a substrate temperature of $450\,°C$, while the target to substrate distance was 5 cm. Before deposition, the chamber was evacuated to a base pressure of 2×10^{-6} Torr and the substrate was cleaned thoroughly by a chemical method. After deposition, the substrates were cooled at $2\,°C\,min^{-1}$ in the same environment as that used during deposition. Similar conditions were maintained for all the oriented substrates. The film thicknesses were 200 nm. To study the crystal structure of Fe_3O_4, a thin-film x-ray diffraction technique was used in $\theta–2\theta$ geometry in the range $15°–80°$ using a Cu Kα radiation source. For the study of the vibrational properties of these films, laser Raman spectroscopy was employed. Raman spectra were recorded at room temperature using a micro-Raman spectrometer (Model HR-800, Jobin Yvon) employing a He–Ne laser ($\lambda = 632.8$ nm). The measured resolution of the spectrometer is $1\,cm^{-1}$. Spectra were collected in backscattering geometry using a charge-coupled device (CCD) with laser power 9 mW and incident laser power focused on a diameter 2 μm. A notch filter was used to suppress the Rayleigh light. The room-temperature magnetic behaviour of these thin films was observed using the vibrational sample magnetometer (VSM) technique (Lakeshore, Model 7401).

3. Results and discussion

Figure 1 shows the x-ray diffraction pattern of a typical Fe_3O_4 thin film on Si(100), (110) and (111) substrates. The XRD patterns reveal the preferred oriented crystalline quality of the Fe_3O_4 films on all the oriented substrates of Si. The preferred orientation of the films is along the [111] direction. We do not detect the presence of any other phase of iron oxide. The calculated lattice parameters of the Fe_3O_4 films are presented in table 1. It should be recalled here that earlier attempts [11–15] to grow Fe_3O_4 films on Si yielded mixed results. Tang *et al* [12] reported the polycrystalline growth of Fe_3O_4 film on Si(100) substrate by the PLD technique. We note that the substrate temperature that they used in their study was $350\,°C$, while in our study it was $450\,°C$. Indeed, the substrate temperature is a very crucial parameter in determining the crystalline quality of Fe_3O_4 film.

We calculated the grain size (D) of the film using the Debye–Scherrer formula given by [16]

$$D = 0.94 \times \lambda/(B \cos\theta)$$

where λ is the wavelength of the x-ray source and B is the full width at half maximum (FWHM) of an individual peak at 2θ (where θ is the Bragg angle). The lattice strain (T) in the material also causes broadening of diffraction peak, which can be represented by the relationship
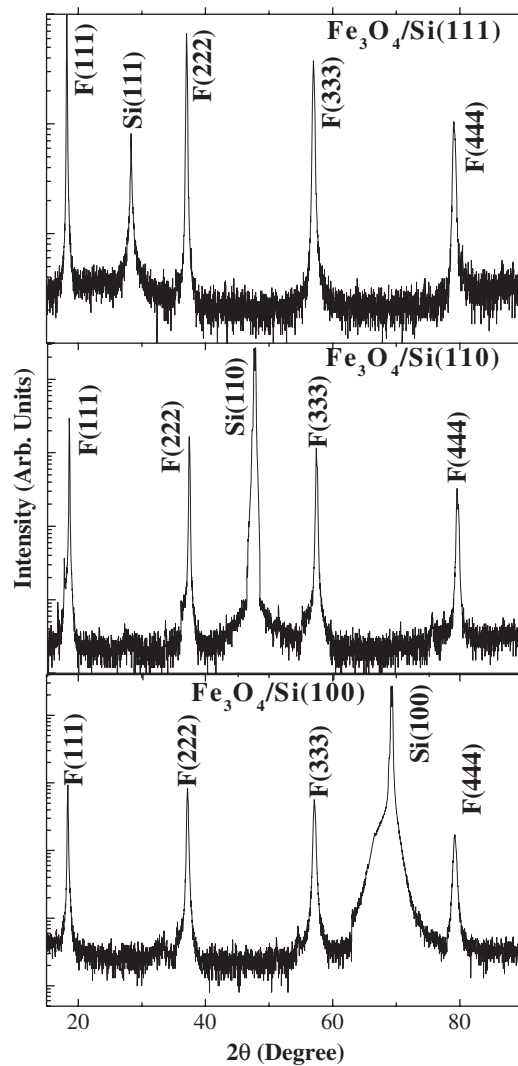
$$T \tan\theta = (\lambda/D \cos\theta) - B.$$

Figure 1. X-ray diffraction pattern for Fe_3O_4 film on Si(100), (110) and (111) substrates.

These parameters are calculated and are shown in table 1. It is clear that film deposited on Si(111) substrate presents the minimum FWHM value and hence the best crystalline quality as compared to other films. We also notice that in all the films the 2θ value for the (111) peak of the film on all substrates remains the same.

Though the XRD patterns suggest the presence of Fe_3O_4 phase in the films, the possibility of the presence of maghemetite cannot be ruled out as their lattice parameters are very close to each other (that for magnetite is $a = 0.8396$ nm while that for maghemetite is 0.8342 nm). To confirm the growth of Fe_3O_4 in the films, we performed Raman spectroscopy measurements, since the vibrational frequencies of both the compositions are different [17] and they can be easily distinguished by Raman spectroscopy. It is known that, at room temperature, the primitive unit cell of Fe_3O_4 contains 14 atoms, and group theory predicts 42 normal modes at
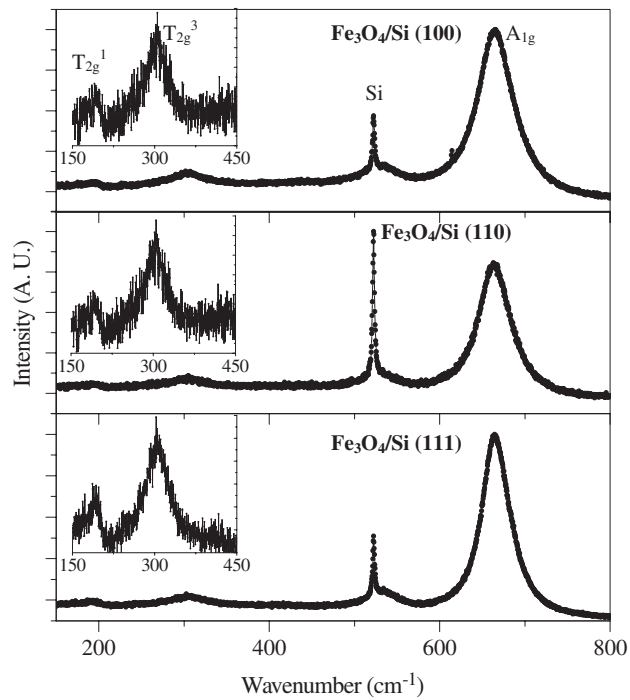
Figure 2. Raman spectra for Fe_3O_4 films deposited on (100), (110) and (111) oriented Si substrates at room temperature. The inset shows the T_{2g}^1 and T_{2g}^3 modes in enlarged scale for individual films.

Table 2. Variation of A_{1g} mode features and coercivity of Fe_3O_4 films on Si substrates.

Substrate	A_{1g} peak position (cm^{-1})	FWHM (cm^{-1})	Coercivity (Oe)
Si(100)	664	51	383
Si(110)	663	47	328
Si(111)	665	41	160

the centre of the Brillouin zone [18].

$$\Gamma = A_{1g} + E_g + T_{1g} + 3\,T_{2g} + 2A_{2u} + 2E_u + 4T_{1u} + 2T_{2u}.$$

In these modes $A_{1g} + E_g + 3T_{2g}$ are Raman-active modes, $4\,T_{1u}$ is an infra-red active mode and the others are silent modes. The A_{1g} mode is the highest frequency mode occurring at 669 cm^{-1}. This mode is obtained by in-phase symmetric stretching of oxygen along the Fe–O bond. The E_g mode occurs at 410 cm^{-1} and T_{2g} modes occur at ($T_{2g}^1 = 193$ cm^{-1}, $T_{2g}^2 = 540$ cm^{-1}, $T_{2g}^3 = 300$ cm^{-1}). In figure 2 we show Raman spectra for all the films. A_{1g}, T_{2g}^1 and T_{2g}^3 modes of Fe_3O_4 and Si substrate peak are present in all films. We show in the inset of figure 2 the modes of T_{2g}^1 and T_{2g}^3 in an enlarged scale for the sake of clarity for all films. To discover the substrate effect on thin films, we have analysed the strongest A_{1g} mode (table 2), keeping in mind that the A_{1g} mode is directly linked to the structure of the magnetite system [19]. It is readily observed that though the peak positions for all the films remain the same, the film on Si(111) possesses the minimum FWHM, suggesting better crystalline quality
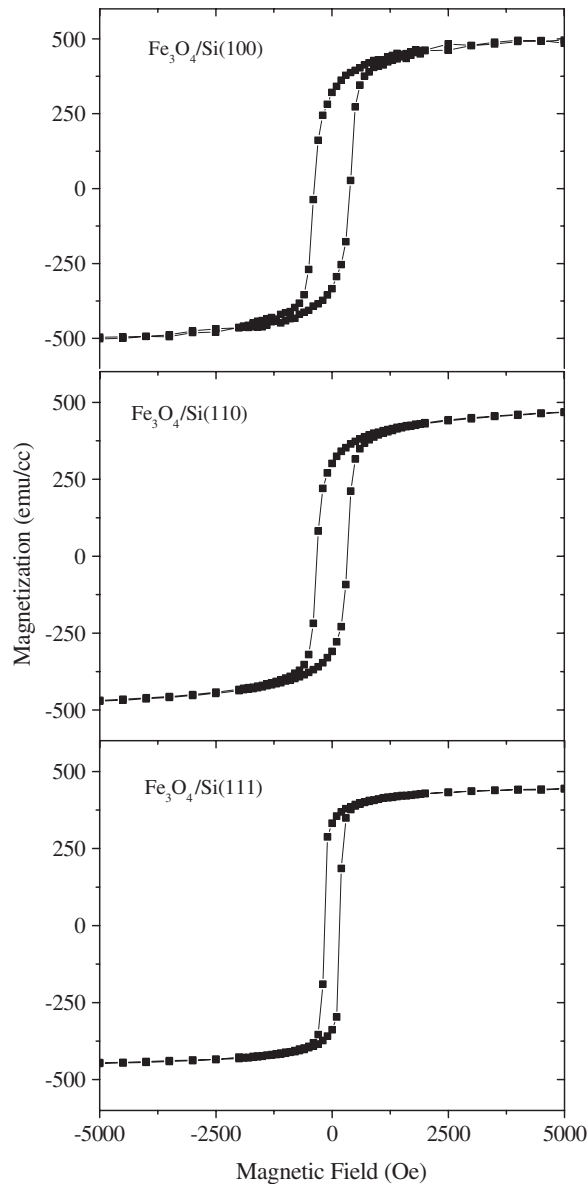
Figure 3. Magnetization hysteresis plots for Fe_3O_4 films deposited on (100), (110) and (111) oriented Si substrates at room temperature.

of the film than others. Indeed, our XRD analysis also indicated the best crystallinity of Fe_3O_4 film on Si(111) substrate.

After ensuring the growth of Fe_3O_4 on Si substrates, we examined these films for their magnetization property. Figure 3 presents the room-temperature magnetization hysteresis behaviour for all samples. We observe a clear hysteresis nature for all samples, suggesting their room-temperature ferromagnetic property. These films demonstrate a tendency of saturation at relatively lower field ($\sim$2000 Oe) than earlier reported saturation fields. It is recalled here that Tang *et al* [12] reported non-saturation of magnetization in pulsed laser deposited Fe_3O_4

thin films on Si(001), which they attributed to the presence of APBs in those nanocrystalline films. However, in the present case we observe that our films are not only highly oriented but also display saturation magnetization. The saturation magnetization for these films is close to that of the single crystal ($\sim$490 emu cm^{-3}) [8]. These results imply that these films are free from APB defects. The calculated coercivity values of these films are shown in table 2. Lower coercivity was obtained in Fe$_3$O$_4$ thin film on Si(111) substrate. In contrast to the earlier report by Jain *et al* [14], we do not require any buffer layer to have bulk-like magnetic behaviour of our thin film.

4. Conclusion

In conclusion, Fe$_3$O$_4$ thin films were deposited on differently oriented Si substrates by the PLD technique. XRD patterns of the films showed the spinel cubic structure with (111) orientation. It was found that the grain size is higher in Fe$_3$O$_4$ thin film on Si(111) substrate. Raman peak positions for all the films remained the same, whereas the A$_{1g}$ peak FWHM value is a minimum in Fe$_3$O$_4$ thin film on Si(111) substrate. These results indicate better crystalline quality in the film on Si(111) substrate. Magnetization results suggest ferromagnetic behaviour for all the films, with saturation magnetization close to that of the single crystal. Further work is in progress to identify the electrical transport properties and structural transition across the Verwey transition point.

Acknowledgments

References

[1] 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
[2] Versluijs J J, Bari M A and Coey J M D 2001 *Phys. Rev. Lett.* **87** 026601
[3] Brabers V A M 1995 *Handbook of Magnetic Materials* vol 8, ed K H J Buschow (Amsterdam: Elsevier Science)
[4] Fabian Z J and Das Sarma S 2004 *Rev. Mod. Phys.* **76** 323
[5] Verwey E J W 1939 *Nature* **144** 327
[6] Leonov I, Yaresko A N, Antonov V N, Korotin M A and Anisimov V I 2004 *Phys. Rev. Lett.* **93** 146404
[7] Shvets I V, Mariotto G, Jordan K, Berdunov N, Kantor R and Murphy S 2004 *Phys. Rev.* B **70** 155406
[8] Margulies D T, Parker F T, Rudee M L, Spada F E, Chapman J N, Aitchison P R and Berkowitz A E 1997 *Phys. Rev. Lett.* **79** 5162
[9] Arora S K, Sofin R G S and Shvets I V 2005 *Phys. Rev.* B **72** 134404
[10] Ogale S B, Ghosh K, Sharma R P, Greene R L, Ramesh R and Venkatesan T 1998 *Phys. Rev.* B **57** 7823
[11] Margulies D T, Parker F T, Spada F E, Goldman R S, Li J, Sinclair R and Berkowitz A E 1996 *Phys. Rev.* B **53** 9175
[12] Tang J, Wang K Y and Zhou W 2001 *J. Appl. Phys.* **89** 7690
[13] Tsai J L, Huang K T, Cheng W C, Lee M D, Chin T S, Jen S U, Lee S F and Yao Y D 2004 *J. Magn. Magn. Mater.* **272–276** 1664
[14] Jain S, Adeyeyea A O and Dai D Y 2004 *J. Appl. Phys.* **95** 7237
[15] Jain S, Adeyeyea A O and Boothroyd C B 2005 *J. Appl. Phys.* **97** 093713
[16] Cullity B D 1972 *Elements of X-Ray Diffraction* (Reading, MA: Addison-Wesley)
[17] Chamritski I and Burns G 2005 *J. Phys. Chem.* B **109** 4965
[18] Gasparov L V, Tanner D B, Romero D B, Berger H, Margaritondo G and Forro L 2000 *Phys. Rev.* B **69** 7939
[19] Gupta R, Sood A K, Metcalf P and Honig J M 2002 *Phys. Rev.* B **65** 104430