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Anomalous magnetic field effects during pulsed injection metal-organic chemical vapor deposition of magnetite films

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We report on large external magnetic field effects during pulsed injection metal-organic chemical vapor deposition of magnetite films on MgO(001). The application of a 1 T field during the growth process significantly increases the saturation magnetization of magnetite by 150%–220% at a deposition temperature of 550 and 600 °C, while the enhancement of the remanent magnetization is even larger. This anomalous magnetic field effect does not drastically alter the crystalline texture, surface morphology, and film thickness of magnetite, but is explained by a suppression of antiphase-boundary formation during film growth. © 2010 American Institute of Physics.

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Magnetite (Fe_3O_4) is a popular magnetic oxide material that has been used in a great number of applications, including electric motors, electromagnets, transformers, video and audio adapters, magnetic inks, and biomedical agents. Moreover, in thin-film form it has recently attracted interest from the spintronics research field where its nearly half-metallic character is explored for spin injection into semiconductors and magnetoresistive structures.^{1–5} Films of Fe_3O_4 have been grown on MgO, Al_2O_3 , Si, GaAs, and other substrates using various deposition techniques including molecular beam epitaxy,^{6–8} pulsed-laser deposition,^{9–12} rf and reactive dc magnetron sputtering,^{13–21} e-beam deposition,²² and ion beam deposition (IBD).²³ The resulting magnetic properties vary considerably due to differences in crystalline texture, stoichiometry, surface morphology, film strain, and lattice defects. Another possible route to tailor the properties of Fe_3O_4 films is the use of a magnetic field during deposition. While this option has not been explored intensively, reports on magnetron-sputtered films indicate that relative modest fields of 30–35 mT can already modify the remanent magnetization and saturation field.^{19,20}

In this paper, we report on the growth of Fe_3O_4 films using pulsed injection metal-organic chemical vapor deposition (PI MOCVD) and we demonstrate that the magnetic properties alter significantly by the application of a 1 T magnetic field during film growth. The observed magnetic field effect is unprecedented and is explained by the formation of less antiphase boundaries in the Fe_3O_4 films. An iron (III) tetramethylheptanodionate $[\text{Fe}(\text{tmhd})_3]$ precursor, inert argon carrier gas, and MgO(001) substrates were used in a single-step PI MOCVD growth process. The temperature of the substrates was kept constant during growth at temperatures ranging from 450 to 600 °C. To facilitate the application of a large magnetic field, a new type of PI MOCVD reactor was constructed inside a switchable 1 T magnet. This reactor was also used to grow films without an external magnetic field. After deposition, the films were slowly cooled in vacuum to

room temperature. For a constant number of deposition pulses (1000 at a frequency of 2 Hz), the Fe_3O_4 film thickness varied with temperature between 20 and 140 nm. This large sensitivity of the deposition rate reflects different precursor decomposition/absorption and diffusion rates within the selected temperature range. Moreover, some variation in film thickness might be explained by gaseous phase turbulences that move the deposition center away from the substrate. The samples in this paper are labeled as follows: “0 T” (no external magnetic field), “1 T” (1 T field during growth and cool down), “cool down 1 T” (1 T field during cool down only).

The lattice constant of Fe_3O_4 ($a=8.397$ Å) is nearly twice as large as that of MgO ($a=4.213$ Å) and thus the lattice mismatch between film and substrate is small. Consequently, it is impossible to detect the $\text{Fe}_3\text{O}_4(004)$ reflection at an expected angle of 43.05° in a conventional θ - 2θ x-ray diffraction scan as it overlaps with the more intense MgO(002) substrate peak at 42.90° . For this reason, x-ray diffraction analysis of Fe_3O_4 films on MgO(001) was conducted by tilting the sample at a ψ angle of 15.79° , which corresponds to the angle between the (001) and (115) lattice planes. In this configuration, unstrained Fe_3O_4 films exhibit a single (115) reflection at a 2θ angle of about 56.93° . Figure 1 shows a summary of the x-ray diffraction results on Fe_3O_4 films that were grown at different temperatures and with and without an external magnetic field. The measurements clearly demonstrate that the films are single crystalline. The position of the (115) reflection is shifted to higher angles (57.1° – 57.4°) with respect to bulk Fe_3O_4 indicating compressive out-of-plane lattice strain in all films. The amount of lattice strain depends nonmonotonously on deposition temperature and it correlates with the variation in film thickness. The application of a 1 T magnetic field during film growth does not drastically alter the crystalline texture of Fe_3O_4 on MgO(001) as illustrated by the negligible changes in the position and width of the (115) reflection for each deposition temperature [black and red data in Fig. 1(b)]. The ϕ scan of the (115) reflection exhibits four peaks of similar intensity which is typical for fully epitaxial films with an in-plane

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FIG. 1. (Color online) (a) θ - 2θ x-ray diffraction scan of Fe_3O_4 on $\text{MgO}(001)$. (b) θ - 2θ x-ray diffraction scans obtained with the sample at a ψ angle of 15.79° . $\text{Fe}_3\text{O}_4(115)$ reflections are shown for films grown at different temperature without (solid lines) and with (squares) an external magnetic field of 1 T. (c) ϕ scan of the $\text{Fe}_3\text{O}_4(115)$ reflection. (d) SEM images of Fe_3O_4 films on $\text{MgO}(001)$. The imaged area is $1.6 \times 1.6 \mu\text{m}^2$.

$\text{Fe}_3\text{O}_4[100]/\text{MgO}[100]$ alignment. All films are gray metallic in color and their electrical resistivity corresponds closely to that of bulk Fe_3O_4 at room temperature.

Figure 1(d) shows selected scanning electron microscopy (SEM) images of Fe_3O_4 films on $\text{MgO}(001)$. The film grown at 450°C (not shown) is smooth and its surface consists of small particle aggregates with an average size of 25–35 nm. The films that were grown at 550 and 600°C possess a similar surface morphology with slightly larger aggregates (40–50 nm). The application of a 1 T field during growth does not affect the Fe_3O_4 films grown below 550°C , but slightly increases the surface roughness at 600°C . We therefore conclude that the application of a 1 T magnetic field during PI MOCVD of Fe_3O_4 does not drastically modify the crystalline texture and the surface morphology.

The magnetic properties of the films were measured using a superconducting quantum interference device (SQUID). Magnetic characterization of the Fe_3O_4 films was carried out at 300 K in a maximum in-plane magnetic field of 1 T. The hysteresis curve of some of the $\text{Fe}_3\text{O}_4/\text{MgO}(001)$ samples was also measured in an out-of-plane magnetic field. The magnetic properties are summarized in Table I and SQUID results for films that were grown at 550°C are shown in Fig. 2. The magnetic hysteresis curves of Fe_3O_4 films on $\text{MgO}(001)$ are rounded and tilted and the remanent and saturation magnetization are small if no magnetic field is used. The application of a 1 T field during film growth drastically alters the magnetic response of the films. The largest effects are obtained at a deposition temperature of 550 and 600°C where the saturation magnetization increases by 150%–220% and the enhancement of the remanent magnetization is even larger. The saturation magnetization for the film grown at 600°C is $457 \times 10^3 \text{ A/m}$, which is close to the Fe_3O_4 bulk value of $471 \times 10^3 \text{ A/m}$.²⁴ The magnitude of

TABLE I. Summary of magnetic properties of PI MOCVD-grown Fe_3O_4 films on $\text{MgO}(001)$.

Deposition temperature	M_S (10^3 A/m)	M_R (10^3 A/m)	$\mu_0 H_C$ (mT)
450, 0 T	82	35	10.0
450, 1 T	107	48	10.0
500, 0 T	166	102 (25 $\pm$)	8.3 (18.5 $\pm$)
500, cool down 1 T	159	94 (27 $\pm$)	14.5 (22.0 $\pm$)
500, 1 T	181	115 (33 $\pm$)	12.0 (21.0 $\pm$)
550, 0 T	191	26 (35 $\pm$)	4.7 (13.0 $\pm$)
550, cool down 1 T	233	52	9.0
550, 1 T	430	161 (124 $\pm$)	11.8 (18.5 $\pm$)
600, 0 T	296	32 (59 $\pm$)	5.2 (15.3 $\pm$)
600, 1 T	457	70 (47 $\pm$)	3.5 (6.0 $\pm$)

the field-induced modifications is unprecedented and somewhat surprising as they do not correlate with clear changes in crystalline texture, surface morphology, and film thickness. To test if an enhancement of film magnetization is only obtained during Fe_3O_4 film growth, we also grew some films without applied magnetic field and subsequently cooled them down to room temperature in 1 T. In this case, a much smaller increase in the remanent and saturation magnetization is observed as illustrated by the triangles in Fig. 2 for a deposition temperature of 550°C . This clearly demonstrates that field-induced changes in the magnetic properties are only partly thermally activated after deposition and thus depend mostly on alterations during the PI MOCVD growth process.

The large influence of deposition temperature and applied magnetic field indicates a significant modification of the magnetic microstructure. Other studies on $\text{Fe}_3\text{O}_4/\text{MgO}(001)$ have shown that the magnetic response is strongly influenced by the formation of antiphase boundary

FIG. 2. (Color online) (a) In-plane and (b) out-of-plane hysteresis curves of Fe_3O_4 films grown at 550°C without (squares) and with (squares) an external magnetic field of 1 T. The triangles illustrate the effect of cooling in a 1 T field. The insets show a magnification of the same data for small magnetic field.

FIG. 3. Dark field TEM images of Fe_3O_4 films on $\text{MgO}(001)$ grown at 550°C . The images were recorded near the $[001]$ direction using the (220) reflection. The Fe_3O_4 film in (a) was grown without a magnetic field and cooled in 1 T and the film in (b) was grown and cooled in a 1 T field. The inset in (b) shows a dark field TEM image of the same film illustrating the formation of a dense network of lattice dislocations when a magnetic field is applied during PI MOCVD.

(APB) networks.^{6–8,14,15} APBs form during the initial stages of film growth when neighboring islands with different Fe_3O_4 symmetry coalesce. Coupling across APBs has been found to vary from ferromagnetic to antiferromagnetic and this can lead to highly complicated magnetic behavior including local out-of-plane moments, superparamagnetism, reduced film magnetization, and saturation fields that can be two orders of magnitude larger than the anisotropy field of bulk Fe_3O_4 . Figure 3 shows plan view transmission electron microscopy (TEM) images of a Fe_3O_4 film that was grown without magnetic field and subsequently cooled in 1 T (left) and a film that was grown and cooled in a 1 T magnetic field (right). The magnetic response of these films corresponds to the triangles and squares curves in Fig. 3(a), respectively. The main TEM images of Fig. 3 were recorded near the $[001]$ direction using dark field contrast and the (220) reflection. Under these conditions, APBs with out-of-plane shift vectors of the $a/4[011]$ type are imaged as dark bands. Obviously, the Fe_3O_4 film that was grown without an external magnetic field exhibits a high density of APBs with irregular shapes. The domain size varies from a few nanometers to about 30 nm and this closely mimics results on magnetron-sputtered Fe_3O_4 films.^{14,15} The application of a 1 T magnetic field during the PI MOCVD growth process drastically reduces the formation of APBs and this results in domains of about 50–100 nm. Moreover, the APBs now coexist with a network of lattice dislocations. This is particularly clear in the inset of Fig. 3, which shows an area with a high density of lattice dislocations and no APBs. TEM analysis of this sample therefore suggests that lattice dislocations are formed because strain relaxation via APBs is no longer sufficient. This contrasts with the results on Fe_3O_4 films that are grown without magnetic field. In the latter case, a dense network of APBs accommodates most of the film stress.

The TEM images of Fig. 3 provide a possible explanation for the anomalous magnetic field effects during Fe_3O_4 film growth. If no field is applied during PI MOCVD, many APBs are formed. Magnetic coupling across the APBs is disturbed and this leads to a complicated magnetic microstructure and reduced film magnetization. Growth in a 1 T external magnetic field, on the other hand, suppresses the

formation of APBs. As a result, the magnetic microstructure is more uniform and the saturation magnetization approaches the Fe_3O_4 bulk value.

In conclusion, we have demonstrated that high-quality Fe_3O_4 films can be successfully grown using a single-step PI MOCVD growth process with a $\text{Fe}(\text{tmhd})_3$ precursor. As one of the main results, it was shown that the application of a 1 T magnetic field during Fe_3O_4 film growth significantly alters the magnetic properties without major changes in crystalline texture, surface morphology, and film thickness. This anomalous behavior is explained by a reduction in APBs as illustrated by TEM analysis. The ability to improve the magnetic properties by an effective suppression of APB formation during Fe_3O_4 growth opens up new approaches toward the fabrication of functional thin magnetic films in external magnetic field.

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¹G. Hu and Y. Suzuki, *Phys. Rev. Lett.* **89**, 276601 (2002).

²G. Hu, R. Chopdekar, and Y. Suzuki, *J. Appl. Phys.* **93**, 7516 (2003).

³S. van Dijken, X. Fain, S. M. Watts, and J. M. D. Coey, *Phys. Rev. B* **70**, 052409 (2004).

⁴S. van Dijken, X. Fain, S. M. Watts, K. Nakajima, and J. M. D. Coey, *J. Magn. Magn. Mater.* **280**, 322 (2004).

⁵E. Snoeck, Ch. Gatel, R. Serra, G. BenAssayag, J.-B. Moussy, A. M. Bataille, M. Pannetier, and M. Gautier-Soyer, *Phys. Rev. B* **73**, 104434 (2006).

⁶T. Hibma, F. C. Voigt, L. Niesen, P. A. A. van der Heijden, W. J. M. de Jonge, J. J. T. M. Donkers, and P. J. van der Zaag, *J. Appl. Phys.* **85**, 5291 (1999).

⁷T. Kasama, R. E. Dunin-Borowski, and W. Eerenstein, *Phys. Rev. B* **73**, 104432 (2006).

⁸S. K. Arora, S. G. S. Sofin, I. V. Shvets, and M. Luysberg, *J. Appl. Phys.* **100**, 073908 (2006).

⁹G. Q. Gong, A. Gupta, G. Xiao, W. Qian, and V. P. Dravid, *Phys. Rev. B* **56**, 5096 (1997).

¹⁰R. J. Kennedy and P. A. Stampe, *J. Phys. D* **32**, 16 (1999).

¹¹D. Reisinger, P. Majewski, M. Opel, L. Alff, and R. Gross, *Appl. Phys. Lett.* **85**, 4980 (2004).

¹²M. Ishikawa, H. Tanaka, and T. Kawai, *Appl. Phys. Lett.* **86**, 222504 (2005).

¹³D. T. Margulies, F. T. Parker, F. E. Spada, R. S. Goldman, J. Li, R. Sinclair, and A. E. Berkowitz, *Phys. Rev. B* **53**, 9175 (1996).

¹⁴D. T. Margulies, F. T. Parker, M. L. Rudee, F. E. Spada, J. N. Chapman, P. R. Aitchison, and A. E. Berkowitz, *Phys. Rev. Lett.* **79**, 5162 (1997).

¹⁵J. F. Bobo, D. Basso, E. Snoeck, C. Gatel, H. Hrabovsky, J. L. Gauffier, L. Ressler, R. Mamy, S. Visnovsky, J. Hamrle, J. Teillet, and A. R. Fert, *Eur. Phys. J. B* **24**, 43 (2001).

¹⁶S. Soeya, J. Hayakawa, H. Takahashi, K. Ito, C. Yamamoto, A. Kida, H. Asano, and M. Matsui, *Appl. Phys. Lett.* **80**, 823 (2002).

¹⁷S. M. Watts, K. Nakajima, S. van Dijken, and J. M. D. Coey, *J. Appl. Phys.* **95**, 7465 (2004).

¹⁸S. M. Watts, C. Boothman, S. van Dijken, and J. M. D. Coey, *Appl. Phys. Lett.* **86**, 212108 (2005).

¹⁹J. P. Hong, S. B. Lee, Y. W. Jung, J. H. Lee, K. S. Yoon, K. W. Kim, C. O. Kim, C. H. Lee, and M. H. Jung, *Appl. Phys. Lett.* **83**, 1590 (2003).

²⁰X.-L. Tang, H.-W. Zhang, H. Su, Z.-Y. Zhong, and Y. Jing, *J. Solid State Chem.* **179**, 1618 (2006).

²¹C. Boothman, A. M. Sánchez, and S. van Dijken, *J. Appl. Phys.* **101**, 123903 (2007).

²²S. Jain, A. O. Adeyeye, and D. Y. Dai, *J. Appl. Phys.* **95**, 7237 (2004).

²³C.-H. Lai, P.-H. Huang, Y.-J. Wang, and R. T. Huang, *J. Appl. Phys.* **95**, 7222 (2004).

²⁴*Magnetic and Other Properties of Oxide and Related Compounds*, edited by K.-H. Hellwege and A. M. Hellwege, Landolt-Börnstein, New Series, Group III, Vol. 4 (Springer, Berlin, 1970).