April 01, 2008

Alternating target laser ablation deposition of high quality barium hexaferrite thin films from barium monoferrite and hematite targets

A. L. Geiler
Northeastern University

S. D. Yoon
Northeastern University

Y. Chen
Northeastern University

A. Yang
Northeastern University

C. N. Chinnasamy
Northeastern University

See next page for additional authors

AIP | Journal of Applied Physics

Alternating target laser ablation deposition of high quality barium hexaferrite thin films from barium monoferrite and hematite targets

A. L. Geiler, S. D. Yoon, Y. Chen, A. Yang, C. N. Chinnasamy et al.

Citation: J. Appl. Phys. **103**, 07B914 (2008); doi: 10.1063/1.2837654
View online: http://dx.doi.org/10.1063/1.2837654
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v103/i7
Published by the American Institute of Physics.

Alternating target laser ablation deposition of high quality barium hexaferrite thin films from barium monoferrite and hematite targets

A. L. Geiler,[a] S. D. Yoon, Y. Chen, A. Yang, C. N. Chinnasamy, M. Geiler, V. G. Harris, and C. Vittoria

Center for Microwave Magnetic Materials and Integrated Circuits, Department of Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts 02115, USA

(Presented on 7 November 2007; received 11 September 2007; accepted 15 November 2007; published online 7 March 2008)

An optimized alternating target laser ablation deposition (ATLAD) technique has been developed to grow high quality barium hexaferrite ($BaFe_{12}O_{19}$) thin films on basal plane oriented sapphire (Al_2O_3) substrates from barium monoferrite ($BaFe_2O_4$) and hematite (α-Fe_2O_3) targets. Crystallographic and structural characterization results show that the films possess low *c*-axis dispersion of $\Delta\omega=0.259°$ and hexagonal terraced surface morphology. Saturation magnetization and uniaxial magnetic anisotropy field were determined to be consistent with reference data on high quality barium hexaferrite films and bulk single crystals grown by other techniques. Ferromagnetic resonance linewidth of 42 Oe was measured at 52 GHz by the shorted waveguide technique. We conclude that the ATLAD technique is capable of growing high quality barium hexaferrite films while providing unique opportunities to control the ionic distribution in the hexagonal unit cell by allowing different species of ions to be introduced from the respective targets in any order and at any time during film growth. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2837654]

INTRODUCTION

Hexagonal ferrites are a technologically important family of ferrimagnetic oxides. Due to their low conductivity, high uniaxial magnetic anisotropy field, and moderate saturation magnetization values, these materials are widely utilized in various microwave, magnetic recording, and permanent magnet applications. The hexagonal crystal structure allows for various ionic substitutions that have been studied extensively in the past.[1–3] These substitutions were shown to affect the magnetic properties of hexagonal ferrites, for instance, the uniaxial magnetic anisotropy field, the coercive field, and the saturation magnetization extending the range of possible applications for these materials.[4]

Pulsed laser deposition (PLD) has long been established as an effective epitaxial growth technique for hexagonal ferrites. Thin barium hexaferrite films deposited by this method were previously shown to possess nearly single crystal crystallographic, magnetic, and microwave properties.[5–7] In the conventional PLD technique, in order to grow thin films of barium ferrite with some of the substitutions outlined above, the same composition needs to be first obtained in an ablation target. High quality films are deposited under optimized growth conditions, such as substrate temperature, pressure, and deposition rate and providing that the film and the substrate are reasonably matched in terms of lattice constants and thermal expansion coefficients. We have recently demonstrated that the hexagonal crystal structures can be grown at the atomic scale from multiple targets possessing different chemical compositions by a technique we refer to as alternating target laser ablation deposition (ATLAD). This technique was previously utilized to deposit hexagonal *M*-type lead ferrite ($PbFe_{12}O_{19}$) thin films on ⟨111⟩ magnesium oxide (MgO) substrates by alternating ablation of tetragonal lead oxide (PbO) and rhombohedral hematite (α-Fe_2O_3) targets.[8] By separating the sources of different species of ions, this technique provides unique opportunities to affect the ionic distribution in the hexagonal unit cell and may enable more selective lattice substitutions.

While the deposition of hexagonal ferrites by the ATLAD technique has already been demonstrated the properties of the resulting films were determined to be inferior to those deposited by the conventional PLD technique, as indicated by the presence of a secondary phase in the films, low saturation magnetization values, and broad ferromagnetic resonance linewidths. In this paper, we present an optimized deposition technique by which high quality barium hexaferrite thin films were grown on ⟨001⟩ Al_2O_3 substrates by alternatively ablating orthorhombic barium monoferrite ($BaFe_2O_4$) and hematite targets. Resulting films were determined to possess crystallographic, magnetic, and microwave properties that were comparable to high quality barium hexaferrite films deposited by the conventional PLD (Refs. 5–7) and other epitaxial growth methods.[9,10]

GROWTH TECHNIQUE

The targets utilized in the deposition of barium hexaferrite films were prepared by the conventional ceramics processing. Approximately 20 g of α-Fe_2O_3 powder was pressed in a 1 in. stainless steel die at 1000 psi and sintered at 1150 °C in a box furnace for 4 h. After sintering, the puck was crushed and grinded in an agate bowl with an assortment of agate balls by a planetary mill. The milling took 4 h at 350 rpm. Resulting powder was mixed with polyvinyl alcohol (PVA) binder and pressed at 2000 psi. After sintering at

[a]Electronic mail: ageiler@ece.neu.edu.

1350 °C for 4 h, a high density (>90%) target was obtained. For the $BaFe_2O_4$ target, approximately 20 g of molar 1:1 mixture of $BaCO_3$ and α-Fe_2O_3 powder was mixed and grinded by a planetary mill at 350 rpm for 4 h. The mixture was pressed at 1000 psi and sintered at 1250 °C for 10 h. The resulting puck was then crushed and grinded as mentioned above. The powder was then mixed with the PVA binder, pressed at 2000 psi, and sintered at 1350 °C for 4 h to obtain a high density target. The chemical compositions of both targets were verified by θ-2θ x-ray diffraction (XRD) using a Cu $K\alpha$ source and energy dispersive x-ray microanalysis and determined to be single phase α-Fe_2O_3 and $BaFe_2O_4$ respectively.

Barium hexaferrite films were deposited on basal plane oriented rhombohedral sapphire (Al_2O_3) substrates. The room temperature lattice mismatch between sapphire and barium hexaferrite film was deduced to be 7% from the comparison of the areas of oxygen planes in both crystal structures.[11] Thermal expansion coefficients were 7.8×10^{-6} ppm/°C (Ref. 12) and 10×10^{-6} ppm/°C (Ref. 13) for sapphire and barium hexaferrite, respectively. The mismatch in thermal expansion coefficients indicates that the films will experience biaxial tensile stress upon cooling down from the deposition temperature of 925 °C. The films were deposited in a high purity oxygen environment of 300 mTorr. A KrF excimer laser with a wavelength of 248 nm, energy of 400 mJ/pulse, and 25 ns full width at half maximum pulse width was focused to an energy density of 10 J/cm^2 on the target surface. The distance between the target and the substrate was set to 5 cm. The rotation of the target carrousel was synchronized with the laser trigger signal to allow the targets to be alternated during film growth and the laser beam to be rastered to maximize target surface usage. The deposition routine consisted of 3 shots on the $BaFe_2O_4$ and 33 shots on the Fe_2O_3 targets. The growth rates from the $BaFe_2O_4$ and the Fe_2O_3 targets were estimated by depositing films from each target on the sapphire substrate under the above conditions to be approximately 1.4 and 0.6 Å/shot, respectively. 300 repetitions of the deposition routine under the conditions described above resulted in an average film thickness of 6500 ± 500 Å measured by a scanning surface profilometer. Upon completion of the deposition process the films were annealed in flowing oxygen in a tube furnace at 1050 °C. To prevent diffusion at the film-substrate interface, the films were rapidly inserted into the preheated furnace, annealed for 20 min, and rapidly removed from the furnace. Annealing of the films beyond the 20 min interval resulted in rapid reduction of the magnetic moment, which was interpreted as evidence of diffusion.

EXPERIMENTAL RESULTS

The crystal structure and orientation of the films was determined by θ-2θ and rocking curve XRD measurements. With the exception of two substrate peaks, only $\langle 002n \rangle$ barium hexaferrite peaks were visible in the θ-2θ spectra, suggesting that the films are single phase and possess a high degree of c-axis orientation.[14] The surface morphology of the films was studied by atomic force microscopy (AFM). A typical AFM micrograph is shown in Fig. 1. A terraced hexagonal structure is clearly visible in the micrograph with individual hexagonal platelets oriented with their surface normal perpendicular to the film plane. This observation is consistent with rocking curve measurements of the $\langle 008 \rangle$ barium hexaferrite peak that revealed full width at half maximum to be $\Delta\omega = 0.259°$, as indicated in the inset of Fig. 1. Rocking curve measurements confirm that the films possess low c-axis dispersion in accord with the AFM measurements.

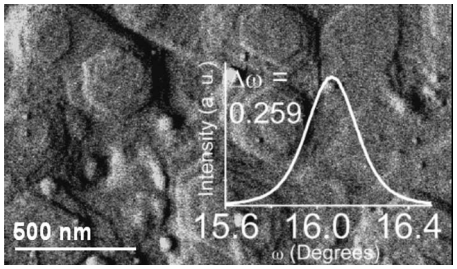

FIG. 1. AFM micrograph of the barium hexaferrite thin film. Rocking curve measurement of the $\langle 008 \rangle$ barium hexaferrite peak (inset).

The static magnetic properties of the films before and after annealing at 1050 °C were studied by vibrating sample magnetometry (VSM) with the magnetic field applied perpendicular and parallel to the film plane. Typical hysteresis loops of the films are shown in the left pane of Fig. 2 for as-deposited films and in the right pane of Fig. 2 for films annealed at 1050 °C for 20 min. As a result of annealing, the saturation magnetization is increased from 3.4 ± 0.2 to 4.6 ± 0.2 kG. The coercive field of the hysteresis loop with the field applied perpendicular to the film plane is decreased from 750 ± 30 to 150 ± 10 Oe. From the saturation field of the nearly linear hysteresis loop with the field applied parallel to the film plane the uniaxial magnetic anisotropy field of 16.5 ± 0.2 kOe was deduced. These magnetic properties are in close agreement with the reference values on high quality barium ferrite films and bulk single crystals found in the literature.[1,2,5–7]

The ferromagnetic resonance (FMR) measurements were carried out by the shorted waveguide technique between 40 and 60 GHz with the static magnetic field applied perpendicular to the film plane. The resonance condition in this configuration is given by

$$f = \gamma'(H_{\text{ext}} + H_A - 4\pi M_S), \tag{1}$$

where H_{ext} is the externally applied magnetic field, H_A is the uniaxial magnetic anisotropy field, $4\pi M_S$ is the saturation magnetization, γ' is the gyromagnetic ratio over 2π, and f is the FMR frequency. A plot of the FMR frequency as a func-

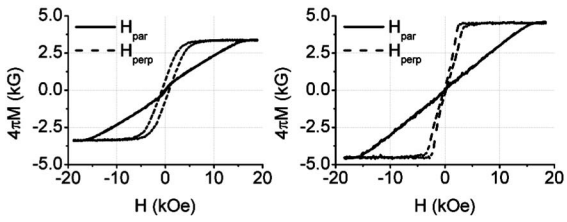

FIG. 2. Hysteresis loops of the barium hexaferrite thin film before (left) and after (right) annealing at 1050 °C for 20 min.

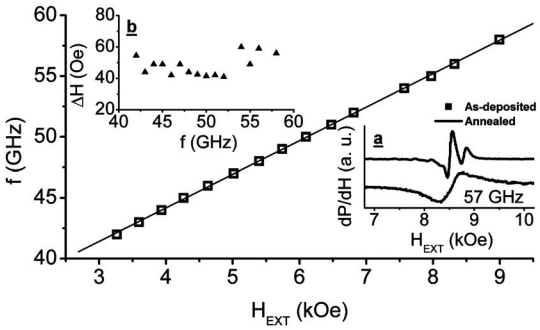

FIG. 3. FMR frequency as a function of the external magnetic field. Main FMR linewidth before and after annealing at 57 GHz [inset (a)]. Main FMR linewidth as a function of frequency [inset (b)].

tion of the externally applied magnetic field is shown in Fig. 3. A linear relationship is observed in agreement with the resonance condition given in Eq. (1). From the linear fit to the experimental data, the gyromagnetic ratio of $\gamma' = 2.795$ MHz/Oe was deduced. From the gyromagnetic ratio, the g-factor of 1.995 was calculated, in close agreement with the reference value on bulk single crystal barium hexaferrite.[1] Sample ferromagnetic resonance spectra obtained at 57 GHz by sweeping the external magnetic field applied perpendicular to the film plane for the films before and after annealing at 1050 °C for 20 min are shown in inset (a) of Fig. 3. By taking the FMR field as the average of the positions of the extrema of the main line for the film after annealing, a value of $H_{\text{ext}}=8.5$ kOe is obtained. Substituting the uniaxial magnetic anisotropy field of $H_A = 16.5 \pm 0.2$ kOe obtained directly from the VSM measurements with the magnetic field applied parallel to the film plane into the resonance condition of Eq. (1) saturation magnetization value of $4\pi M_S = 4.6 \pm 0.2$ kG is obtained, in close agreement with the value calculated from the VSM measurements by taking into account the magnetic volume of the film. Broad FMR linewidth of $\Delta H = 500 \pm 50$ Oe is observed in the as-deposited films. After annealing, the FMR linewidth is improved by a factor of 10 to $\Delta H = 50 \pm 5$ Oe. Multiple spin wave mode excitations are visible in the FMR spectra of the films after annealing on the low field side of the main FMR line, indicative of the magnetic homogeneity of the films. A detailed analysis of the spin wave resonance spectra is outside of the scope of the current treatment and will be presented elsewhere. The mode on the high field side of the main FMR line may be due to a surface mode excitation or an interfacial mode excitation due to variation in the internal field at the film-substrate interface. A plot of the FMR linewidth as a function of frequency is shown in inset (b) of Fig. 3. Narrowest FMR linewidth of 42 Oe was measured at 52 GHz, compared to the linewidth of 23 Oe reported in the literature for high quality barium hexaferrite thin films deposited by the single target PLD technique.[5,6]

DISCUSSION AND CONCLUSIONS

Thin films of barium hexaferrite were deposited on basal plane oriented sapphire substrates by ATLAD of barium monoferrite and hematite. XRD measurements show that the films are single phase with good basal plane orientation and low c-axis dispersion, which is indicative of high degree of epitaxy in the films. AFM measurements show that the films possess hexagonal terraced morphology with individual hexagonal platelets aligned with their surface normal perpendicular to the film plane.

The effects of annealing on the magnetic and microwave properties of the films were studied by VSM and FMR measurements, respectively. After annealing, the films were determined to possess saturation magnetization and uniaxial magnetic anisotropy values that agreed well with reference data on thin films and bulk single crystals of barium hexaferrite. Ferromagnetic resonance linewidth of 42 Oe was measured at 52 GHz compared with the linewidth of 23 Oe measured for high quality barium hexaferrite films deposited by the single target PLD technique.[7]

We therefore conclude that high quality barium hexaferrite thin films can be grown by alternatively ablating targets of different chemical compositions. The ATLAD technique holds great promise for studying the effects of various lattice substitutions on the magnetic and microwave properties of hexagonal ferrites. By allowing control over the amount of various ions and the order in which they are introduced during film growth simply by varying the number and the timing of laser shots on the respective targets in the deposition routine, this technique may provide unique opportunities to control the ionic distribution in the hexagonal unit cell.

ACKNOWLEDGMENTS

This research was supported by the Office of Naval Research under Grant No. N00014-05-1-0349 and the National Science Foundation under Award No. DMR-0400676.

[1] *Magnetic and other properties of oxides and related compounds*, Landolt-Börnstein, New Series, Vol. 4, Pt. B, edited by K. H. Hellwege and A. M. Hellwege (Springer, Berlin, 1970), pp. 562–583.
[2] J. Smit and H. P. J. Wijn, *Ferrites* (Wiley, New York, 1959), pp. 177–211.
[3] G. Albanese and A. Deriu, Ceramurgia Int. **5**, 3 (1979).
[4] D. B. Nicholson, Hewlett-Packard J. **41**, 59 (1990).
[5] S. D. Yoon, C. Vittoria, and S. A. Oliver, J. Appl. Phys. **92**, 6733 (2002).
[6] Y. Song, S. Kalarickal, and C. E. Patton, J. Appl. Phys. **94**, 5103 (2003).
[7] L. V. Saraf, S. E. Lofland, A. V. Cresce, A. P. Monga, S. M. Bhagat, and R. Ramesh, IEEE Trans. Magn. **37**, 2377 (2001).
[8] A. Geiler, Y. He, S. D. Yoon, A. Yang, Y. Chen, V. G. Harris, and C. Vittoria, J. Appl. Phys. **101**, 09M510 (2007).
[9] S. D. Yoon and C. Vittoria, J. Appl. Phys. **96**, 2131 (2004).
[10] R. Karim, K. D. McKinstry, J. R. Truedson, and C. E. Patton, IEEE Trans. Magn. **28**, 3225 (1992).
[11] M. S. Yuan, H. L. Glass, and L. R. Adkins, Appl. Phys. Lett. **53**, 340 (1988).
[12] *CRC Materials Science and Engineering Handbook*, edited by J. F. Shackelford (Chemical Rubber, Boca Raton, FL, 1994), pp. 308–314.
[13] P. C. Dorsey, S. B. Qadri, J. L. Feldman, J. S. Horwitz, P. Lubitz, D. B. Chrisey, and J. B. Ings, J. Appl. Phys. **79**, 3517 (1996).
[14] A. L. Geiler, S. D. Yoon, Y. Chen, C. N. Chinnasamy, Z. Chen, M. Geiler, V. G. Harris, and C. Vittoria, Appl. Phys. Lett. **91**, 162510 (2007).