Growth and characterization of thick oriented barium hexaferrite films on MgO (111) substrates

S. A. Oliver* a)
Center for Electromagnetic Research, Northeastern University, Boston, Massachusetts 02115

S. D. Yoon, I. Kozulin, b) M. L. Chen, and C. Vittoria
Department of Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts 02115

(Received 14 February 2000; accepted for publication 13 April 2000)

Highly oriented films of BaFe$_{12}$O$_{19}$ have been deposited onto MgO (111) substrates by pulsed laser ablation deposition. In contrast to epitaxial BaFe$_{12}$O$_{19}$ films grown on Al$_2$O$_3$ (001) substrates, these films experience an in-plane biaxial compressive stress, and do not crack or delaminate to thicknesses of at least 28 µm. X-ray diffraction, magnetometry, torque magnetometry, and ferromagnetic resonance results all indicate excellent c-axis orientation normal to the film plane, and magnetic properties comparable to bulk values. The thickness and properties of these films approach those required for applications in low-loss self-biased nonreciprocal microwave devices. © 2000 American Institute of Physics. [S0003-6951(00)01324-3]

One critical concern during the growth of the thick (>25 µm) highly oriented films of ferrimagnetic hexaferrite materials that are needed for planar nonreciprocal microwave devices is the control of the deleterious effects of large thermally induced biaxial stresses. Since the stress relationship in epitaxial films is intimately tied to the differences between the lattice parameters and coefficients of thermal expansion of the film and underlying substrate, it is essential that these differences be minimized in order to avoid film cracking and delamination. However, in contrast to the film growth conditions that can be varied systematically, such as the substrate temperature, ambient atmosphere, target stoichiometry, etc., the number of substrates that have physical parameters complementary to the hexaferrites is severely limited due to crystallographic and economic considerations.

The present development of epitaxial hexaferrite films, such as barium hexaferrite (BaFe$_{12}$O$_{19}$), has exclusively examined films deposited onto sapphire (Al$_2$O$_3$) substrates having various crystallographic orientations. Here sapphire has the rhombohedral (corundum) structure that reasonably well matches the lattice parameters of BaFe$_{12}$O$_{19}$, which itself consists of a hexagonal close packed structure of oxygen planes, where the magnetic cations are present at interstitial sites. The room temperature lattice mismatch has been estimated at 7% for (001) BaFe$_{12}$O$_{19}$ films deposited on (001) Al$_2$O$_3$, where it has been noted that a significant shear strain is also present at the interface due to the mismatch in crystallographic lattices. More importantly for thick film growth, the coefficient of thermal expansion of (001) Al$_2$O$_3$ at 7.80 $10^{-6}$ °C$^{-1}$ for 0°C–927°C is less than that of BaFe$_{12}$O$_{19}$ (5 $10^{-6}$ °C$^{-1}$), such that the BaFe$_{12}$O$_{19}$ films sustain significant biaxial tensile stress upon cooling from the deposition temperature of 900–925°C. These large stresses are manifested through the fracture and delamination of the films, where the delamination is observed to occur either through spalling in the film, spalling in the substrate, or debonding at the interface. In practice, the maximum attainable thickness of BaFe$_{12}$O$_{19}$ (001) films on Al$_2$O$_3$ (001) substrates is less than 20 µm, which yields films that are too thin for practical application in low-loss microwave devices operating at frequencies below 40 GHz.

In order to develop the thick oriented hexaferrite films required for microwave devices, we have deposited and characterized the properties of BaFe$_{12}$O$_{19}$ films grown on (111) MgO substrates by pulsed laser ablation deposition. Here, the ionic MgO crystalline lattice has a face centered cubic structure, such that the MgO (111) crystal plane is close packed and retains the continuity of oxygen planes from the (001) BaFe$_{12}$O$_{19}$ film. Thus, from straightforward geometrical considerations it is expected that the BaFe$_{12}$O$_{19}$/MgO system indicates stress relationship for the BaFe$_{12}$O$_{19}$/MgO film. The crystal axis will lie collinear to the [110] axis in the MgO (111) crystal plane. The lattice parameter of MgO is $a_{MgO}$ = 4.213 Å, such that a lattice mismatch of $e = (a_{BaM} - a_{MgO})/a_{BaM} = 0.01$ is expected between atoms on the MgO (111) plane and those of (001) BaFe$_{12}$O$_{19}$ ($a_{BaM} = 5.893$ Å). More importantly, the measured thermal expansion coefficient of MgO (13.6 $10^{-6}$ °C$^{-1}$) is greater than that of BaFe$_{12}$O$_{19}$, such that the barium hexaferrite film will experience biaxial compressive stress upon cooling. Now the stress relationship for the BaFe$_{12}$O$_{19}$/MgO system indicates that the ultimate obtainable film thickness will be governed by the fracture strength of the MgO substrate instead of the BaFe$_{12}$O$_{19}$ film.

The barium hexaferrite films characterized here were typically deposited onto 0.5 mm thick (111) MgO substrates by pulsed laser ablation deposition using a KrF excimer laser ($\lambda = 248$ nm) at an energy density of 4–5 J/cm$^2$ and a repetition rate of 50 Hz. The ambient oxygen pressure was set at 20 mTorr, which corresponds to the optimal pressure found for growth of thick BaFe$_{12}$O$_{19}$ films on Al$_2$O$_3$ (001) substrates. The substrate temperature was maintained at either 900 or 925°C, where an in situ halogen lamp was used in addition to a conductive heater in order to maximize the
temperature of the film surface temperature throughout the deposition. Targets consisted of 2 in. diam pressed powder and sintered BaFe$_{12}$O$_{19}$, which were mounted 4 cm from the substrate and rotated and rastered to maximize target surface usage. All films were observed to be dense and void free from cross-sectional electron micrographs, with the film thicknesses ranging from 1 to 28 μm. Selected films were characterized by x-ray diffraction, magnetometry, torque magnetometry, and ferrimagnetic resonance measurements.

X-ray diffraction measurements were obtained using a Bragg–Bretano powder diffraction system. Figure 1 shows the diffraction pattern obtained on a 1 μm thick BaFe$_{12}$O$_{19}$ film, where the observed peaks have been labeled by the Miller indices for both MgO and BaFe$_{12}$O$_{19}$. All of the International Center for Diffraction Data listed BaFe$_{12}$O$_{19}$ (00n) peaks are present in this pattern, along with the (0,0,22) peak that does not appear in standard databases. A value for the c-axis lattice parameter of c = 23.290 Å was found by fitting the centroids of the four tallest (00n) peaks to the Bragg diffraction equation. This value is greater than either the c-axis values for bulk BaFe$_{12}$O$_{19}$ or for those of films deposited under identical growth conditions onto (00n)Al$_2$O$_3$, and is thus suggestive that the c-axis lattice parameter is affected by the biaxial compressive stress. However, both oxygen defects and stacking faults may also contribute to this effect. A similarly enlarged c-axis lattice parameter was also found from the diffraction pattern for a 16 μm film, where this film showed only Al$_2$O$_3$(00n) and highly broadened BaFe$_{12}$O$_{19}$(00n) peaks.

Excellent magnetic orientation was observed for these films from magnetometry and torque magnetometry measurements. Figure 2 shows the hysteresis loop behaviors for a 27 μm film where the applied field $H$ was oriented either in the film plane (||) or normal to the film surface (⊥). Both results demonstrate the excellent magnetic orientation present in this film, which arises because the magnetic easy axis of BaFe$_{12}$O$_{19}$ coincides with the crystallographic c axis. Here the normal measurement shows the good square loop behavior expected when the magnetic easy axis lies out of the film plane, where the hysteresis curve is skewed due to the demagnetizing field internal to the film. A mean value for the volume saturation magnetization for these films of 4 $\pi M_s = 4.2 \pm 0.2$ kOe was obtained from the demagnetizing field values and magnetic moments by averaging over five films having thicknesses above 20 μm. Meanwhile, the in-plane hysteresis curve shows the linear approach to saturation expected for a highly oriented crystal where the uniaxial anisotropy field value $H_A$ exceeds the 12.5 kOe measurement field.

Torque magnetometry results also confirmed the excellent magnetic orientation present for these BaFe$_{12}$O$_{19}$ films. Figure 3 shows the magnetic torque versus rotation angle for a 1.7 μm film where the film is rotated both clockwise and counterclockwise around an axis in the film plane in an applied field of 10 kOe. A distinct uniaxial symmetry is apparent for both curves, where $H$ lies normal to the film plane near 10° and 190°, and the difference between rotation directions is apparent at angles near the magnetically hard in-plane orientation since $H$ has insufficient intensity to align the magnetization into the film hard plane. In contrast, measurements that are taken with $H$ rotating in the film plane show no discernable variations in torque with film in-plane angle, indicating that there is no preferential component of in-plane anisotropy.

The microwave magnetic properties of thinner films were appraised by ferrimagnetic resonance (FMR) measurements obtained using a shorted waveguide technique at fre-
quences from 40 to 60 GHz. Figure 4 shows the differential power absorption $dP/dH$ vs $H$ for a 1.7 μm film at a frequency of 54 GHz. This resonant absorption shows a FMR linewidth of $\Delta H = 0.70$ kOe, which is considerably larger than the best previous values of $\Delta H = 0.035 - 0.070$ kOe found for BaFe$_{12}$O$_{19}$ films on (001)Al$_2$O$_3$ substrates.\textsuperscript{3,13} However, the resonant absorption mode for these films is expected to be highly broadened compared to the reference films since these films contain more strains and defects due to their much higher growth rate and much lower ambient oxygen growth pressure, and due to the localized spin pinning and demagnetizing field effects caused by the outgrowths that appear on the thicker films. The uniaxial anisotropy field for this film was found to be $H_A = 16.4$ kOe by fitting the resonance equation to the measured frequency vs resonant field results, where the Lande $g$ factor was taken as 2.00.\textsuperscript{3} This value for $H_A$ is also lower than the bulk value of $H_A = 17.6$ kOe,\textsuperscript{14} but is similar to the values found for films deposited on Al$_2$O$_3$(001) substrates.\textsuperscript{12}

The usefulness of these BaFe$_{12}$O$_{19}$ films can be further enhanced through methods such as reducing the FMR linewidth, depositing thicker films, or through cation substitution to modify the magnetic properties. Reductions in the FMR linewidth can be obtained through annealing procedures that refine the crystal structure and remove defects. For example, the FMR linewidth was found to decrease from 0.45 to 0.35 kOe for a 1 μm film after calcining at 1000 °C for 2 h. However, based upon the previous results found for BaFe$_{12}$O$_{19}$ films on Al$_2$O$_3$, it may be necessary to grow films at much higher oxygen pressures than those considered here in order to obtain markedly better FMR linewidths.\textsuperscript{3,13}

As noted above, the usage of MgO as a substrate now means that the ultimate usable film thickness is governed by the fracture strength of the substrate. Fortunately, bimetallic strip models of layered structures having comparable thicknesses indicate that the stress internal to the substrate can itself be controlled through the choice of substrate thickness,\textsuperscript{15} thus providing a method for forestalling fractures in the substrate that might otherwise hinder the growth of thick BaFe$_{12}$O$_{19}$ films. Finally, the usefulness of thick BaFe$_{12}$O$_{19}$ films can be extended to microwave devices operating over many different frequency ranges through compositional adjustment of the film uniaxial anisotropy field through the substitution of nonmagnetic cations for iron within the magnetic lattice.\textsuperscript{16}

The authors would like to thank P. Shi for assistance with the FMR measurements. This research was supported by the Office of Naval Research and the Defense Advanced Research Projects Agency under the 1996 Multidisciplinary University Research Initiative.

\begin{figure}[ht]
\centering
\includegraphics[width=0.5\textwidth]{fig4}
\caption{A ferrimagnetic resonance spectra taken on a 1.7 μm film at 54 GHz is shown, where $\Delta H$ is the ferrimagnetic linewidth.}
\end{figure}

\textsuperscript{12} International Centre for Diffraction Data (ICDD) card number 43-1022.
\textsuperscript{13} International Centre for Diffraction Data (ICDD) card numbers 39-1433 and 43-0002.