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Microstructural and ferromagnetic resonance properties of epitaxial nickel ferrite films grown by chemical vapor deposition

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Microstructural and ferromagnetic resonance properties of epitaxial nickel ferrite ($NiFe_2O_4$) films grown by direct liquid injection chemical vapor deposition are reported. While high-quality epitaxial growth of $NiFe_2O_4$ films on (100)-oriented $MgAl_2O_4$ substrate is confirmed by high resolution transmission electron microscopy, bright field (diffraction contrast) TEM studies reveal the presence of dislocations and also dark diffused contrast areas, which originate from antiphase domains. Angle and frequency-dependent ferromagnetic resonance (FMR) experiments are conducted to determine the magnetic anisotropy and the magnetic relaxation. A low out-of-plane FMR linewidth of ~160 Oe has been observed at a frequency of 10 GHz. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4754847]

Epitaxial thin films of spinel ferrites are attracting interest because of their unique physical properties that can be utilized in layered magnetoelectric heterostructures and spintronic devices.[1–5] Generally, these properties can be tuned by many factors, such as thin film strain, surface morphology, microstructure, and chemical composition, etc., which are closely related to the specific growth method and process conditions. For nickel ferrite ($NiFe_2O_4$) and other insulating ferrite thin films, magnetic damping is one of the important properties to be considered for practical applications, such as in planar microwave devices and magnetic memory elements. The magnetic damping characteristics can be determined by ferromagnetic resonance (FMR) experiments.[6–10] Both experimental and theoretical studies of the ferromagnetic resonance properties of bulk single crystalline nickel ferrite have been reported by different groups dating back to the 1950s.[11,12] However, detailed FMR studies on epitaxial nickel ferrite thin films are quite rare.[6,13] One of the main reasons is the difficulty to fabricate high quality, homogeneous epitaxial films with limited surface and bulk defects exhibiting a narrow FMR linewidth. So far, only few deposition methods with follow-up FMR characterization have been reported.[6,13] Structural and magnetic properties of epitaxial nickel ferrite films on MgO substrate by both chemical transport and reactive sputtering have been reported by Schröder *et al*.[6] Relatively broad in-plane FMR linewidth (700–1700 Oe) and unresolved out-of-plane FMR curves have been observed. In a more recent study by Chinnasamy *et al*., post-deposition thermal annealing (1000 °C) of epitaxial nickel ferrite films grown by pulsed laser deposition has been found to effectively decrease the out-of-plane FMR linewidth from 1500 to 330 Oe.[13] The redistribution of Ni^{2+} ions between tetrahedral and octahedral sites has been suggested as the primary reason for this decrease. In spite of these relevant studies, the linewidth value of as-grown films is still not satisfactory as compared to that of bulk crystals of nickel ferrite (40–80 Oe).[14] Using metal β-diketonate chemical precursors and (100)-oriented $MgAl_2O_4$ substrates for a direct liquid injection chemical vapor deposition (DLI-CVD) process, we have recently reported on the growth of nearly stoichiometric epitaxial thin films that are atomically smooth and with excellent static magnetic properties.[15] In this letter, both the microstructural features using TEM and FMR properties of the films are reported.

Epitaxial nickel ferrite films are grown on $MgAl_2O_4$ (100) substrates by the DLI-CVD technique using anhydrous metal acetylacetonates ($Ni(acac)_2$ and $Fe(acac)_3$) as precursors. A vaporization system (DLI-200/Brooks instruments) is used to vaporize the precursors $Ni(acac)_2$ and $Fe(acac)_3$ in a molar ratio of 1 to 2 dissolved in the solvent *N*,*N*-dimethylformamide (DMF). Vapor of the precursors can be generated at relatively low temperatures (150–175 °C) and the feeding rate of precursors into the reaction chamber can be accurately controlled by a liquid mass flow controller. Films are deposited in a 1.5-in. diameter horizontal quartz tube reactor under deposition pressure of ~12 Torr. Ultra high purity oxygen and argon are used as the oxidant and vapor carrier gas, respectively. Atomically polished (100)-oriented $MgAl_2O_4$ substrates (5 mm×5 mm) with a thickness of ~0.5 mm are ultrasonically cleaned in acetone and isopropanol sequentially before being loaded into the deposition chamber. The nickel ferrite films deposited at different temperatures (500 to 800 °C) have been characterized for surface morphology, chemical composition, crystal structure, and static magnetic properties, the details of which have been reported elsewhere.[15] While the films show improved crystalline quality and higher saturation magnetization with increasing deposition temperature, those deposited at a substrate temperature of 600 °C exhibit the lowest FMR linewidth for both in-plane (external field parallel to the film plane) and out-of-plane (external field perpendicular to the film plane) FMR measurements. Samples deposited at 500 °C show similar out-of-plane FMR linewidth, but the curve shape is distorted due to convolution of multiple peaks, which might be attributed to the excitation of perpendicular standing spin wave modes. In this communication, only results from films

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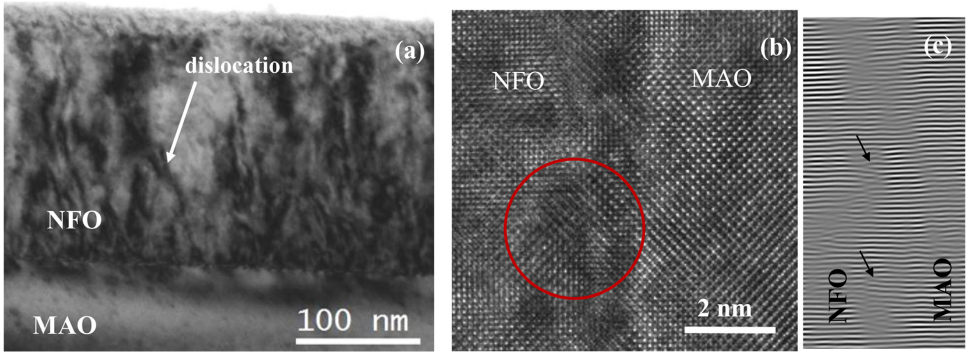

FIG. 1. TEM images from NFO grown on (100)-oriented $MgAl_2O_4$ substrate showing microstructural defects present in the film. (a) Bright field TEM image with $g = \langle 220 \rangle$, presence of threading dislocations and dark diffused contrast can be observed, (b) HRTEM image and (c) Fourier filtered image with $g = \langle 004 \rangle$ showing formation of misfit dislocations.

deposited at 600 °C with a nominal thickness of 0.78 μm, surface roughness of ~0.3 nm (rms, 5 μm×5 μm) and chemical composition of $Ni_{0.98}Fe_{2.02}O_4$ are reported. From x-ray measurements, the studied films are determined to have lattice parameters close to that of the bulk (0.834 nm) with essentially complete strain relaxation.[15]

Transmission electron microscopy (TEM) is used to examine the thin film crystal quality and probe for microstructural defects that can influence the FMR properties. TEM bright field ($g = \langle 220 \rangle$) and high resolution TEM (HRTEM) images from nickel ferrite film grown on $MgAl_2O_4$ (100) are shown in Figs. 1(a) and 1(b), respectively. Threading dislocations and dark diffused contrast areas are seen in Fig. 1(a). These dislocations are likely generated during the thin film strain relaxation process caused by lattice mismatch or thermal expansion difference between the film and substrate. It has been reported by Mitlina *et al.*[16] that the density and distribution of dislocations in spinel ferrite films can influence the crystalline and induced uniaxial anisotropy constants. The dark diffused contrast in some regions of the TEM and HRTEM images in Figs. 1(a) and 1(b) results from antiphase domains, with different cation ordering observed in these regions of the film as reported by Datta *et al.*[17,18] The density of antiphase boundaries (APBs) has been related to the degree of lattice mismatch between film and substrate,[17] and high density of APB can result in rounded hysteresis loops with large saturation fields and reduced magnetization (M_S).[19] For our nickel ferrite films, a M_S value of ~260 emu/cc has been observed, which is lower than the bulk value of 300 emu/cc and can be partly attributed to the presence of APBs. The HRTEM image in Fig. 1(b) shows the atomic structure near the interface area and a Fourier filtered image ($g = \langle 004 \rangle$) of this area is shown in Fig. 1(c). Misfit dislocations are observed at the interface as marked with black arrows in Fig. 1(c). However, no misoriented grains are visible in all the acquired images, indicative of the formation of a high quality epitaxial nickel ferrite layer.

The frequency dependence of the FMR resonance field and linewidth, with the external field oriented along different crystal orientations, are shown in Figs. 2(a) and 2(b), respectively. Because of the demagnetizing field, the hard axis is aligned out of the film plane along the [001] direction. A small difference in the FMR mode positions between the in-plane directions of [100] and [110] is observed, which is caused by the magnetocrystalline anisotropy of the cubic nickel ferrite. Noteworthy, the anisotropy can be influenced by the density and distribution of dislocations, as observed in Fig. 1(a). The true easy axis for bulk single crystal of nickel ferrite has been reported to be along the [111] direction.[11,12] The influence of crystalline anisotropy on the resonance field has been studied by Macháčková *et al.* based on an effective internal field method.[20] Assuming zero in-plane demagnetization fields and only accounting for the first order magnetocrystalline anisotropy K_1, we have estimated the related magnetic parameters. The values of g (spectroscopic splitting factor) and magnetocrystalline anisotropy field ($2K_1/M_S$) are 2.27 (±0.01) and −228 (±46) Oe, respectively. The fact that the g value is larger than 2 and a negative K_1 constant for nickel ferrite single crystal have been reported previously.[11,12] The effective magnetization $4\pi M_{eff}$ is determined to be 2560 (±46) G, which is somewhat lower than the saturation magnetization ($4\pi M_S$) value of ~3280 G (±5%) measured by vibrating sample magnetometry (VSM).[15]

As seen in Fig. 2(b), frequency dependence of the FMR linewidth shows variations with field orientation. The

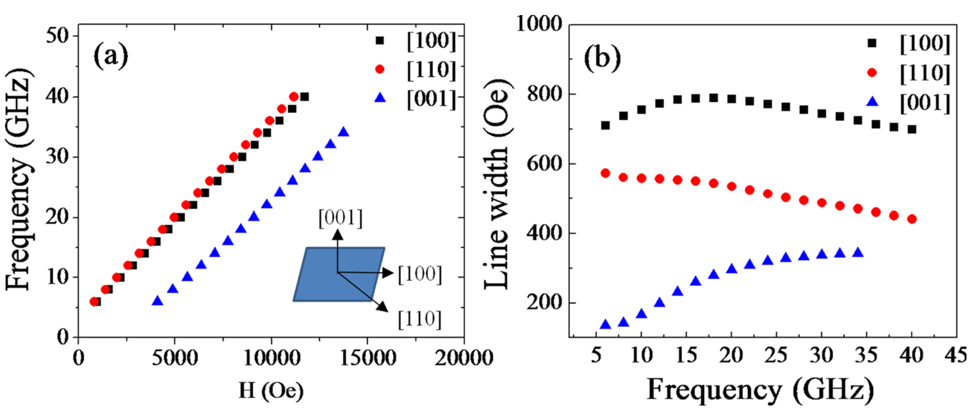

FIG. 2. (a) FMR resonance field and (b) linewidth at different microwave frequencies and static field orientations.

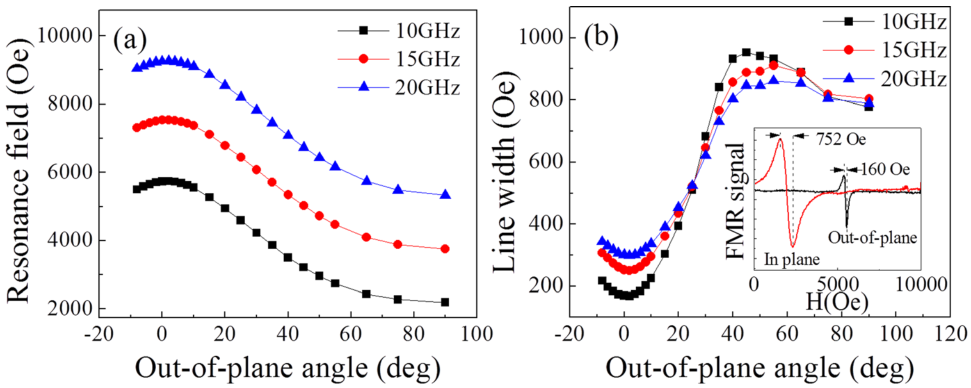

FIG. 3. Angular and frequency dependence of (a) FMR resonance field and (b) linewidth. The inset in (b) shows the in-plane and out-of-plane FMR curves measured at 10 GHz.

in-plane measurements (along [100] and [110]) show relatively larger FMR linewidths than the out-of-plane ([001]) measurement. This is consistent with the presence of crystalline defects leading to two-magnon scattering losses. A linewidth peak at around ~16 GHz for the [100] direction is observed. A possible damping mechanism to generate this linewidth peak feature is a "slow relaxer," as reported by Torres *et al.*[14] However, no peaks as a function of frequency are observed for the other two orientations, and thus we can likely rule out this mechanism. The linewidth profile of the [001] direction, which is an out-of-plane measurement, does not contain any two-magnon scattering contribution. The lowest peak-to-peak FMR linewidth value as shown in Fig. 2(b), at 6 GHz, is $\Delta H_{PP} = 135$ Oe. We note that VSM measurements show that the films only gradually reach saturation at fields above 10 kOe,[15] which likely explains the unusual behavior of the linewidth for low frequencies, in particular for the in-plane measurements.

The FMR resonance field and linewidth dependence as a function of elevation angle are shown in Fig. 3. At the three measured microwave frequencies, 10, 15, and 20 GHz, the FMR resonance fields show essentially similar trends as the magnetic field direction with respect to the film normal is varied from 0° to 90° (Fig. 3(a)). The observed elevation angle dependence is primarily caused by the demagnetization field. While the resonance field displays a near-monotonic profile, the FMR linewidth shows a broad peak feature with the maximum FMR linewidth at around 45° for all three microwave measurement frequencies (Fig. 3(b)). The FMR spectra of films measured at 10 GHz for both in-plane and out-of-plane orientation are shown as inset in Fig. 3(b). The out-of-plane FMR linewidth value of $\Delta H_{PP} = 160$ Oe at 10 GHz is significantly lower than those reported previously for nickel ferrite films.[6,13]

Practical applications of nickel ferrite films in microwave devices, such as band-pass filters, phase shifters, and delay lines, require low microwave losses. Pulsed laser deposition (PLD) is a well established technique for the growth of spinel ferrite thin films that can help retain the stoichiometry of the target material over a wide range of process conditions. Nevertheless, so far, the best reported out-of-plane FMR linewidth of PLD grown nickel ferrite films is around 1500 Oe. This value is about 10 times higher than that of our DLI-CVD grown films. Moreover, a potential advantage of DLI-CVD over the PLD technique is high film growth rate, which is important for the growth of relatively thick films (>1–10 μm) necessary for microwave applications. For films reported here, the growth rate is around 20 nm/min, and the rate can be further increased by increasing the liquid precursor injection rate and optimizing the corresponding vaporization conditions.

In summary, epitaxial growth of nickel ferrite films on $MgAl_2O_4$ (100) substrates by the DLI-CVD technique leading to relatively low FMR linewidth has been demonstrated. In spite of the presence of microstructural defects as observed by bright field TEM, high-quality epitaxial growth has been confirmed by HRTEM. Angular and frequency-dependent study of the FMR linewidth suggests the presence of two-magnon scattering as a magnetization damping mechanism. This is primarily related to crystalline defects and inhomogeneities, including dislocations, anti phase boundaries, and different cation ordering. A low FMR linewidth of ~160 Oe has been achieved at 10 GHz, which confirms the good crystalline quality of DLI-CVD nickel ferrite films. Further improvement in the FMR linewidth will likely require growth of the ferrite films on isostructural spinel substrates with much better lattice match in order to further reduce the density of microstructural defects.

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