Stress-induced anisotropy in LPE grown Ni(Fe,Al)2O4 films

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STRESS-INDUCED ANISOTROPY IN LPE GROWN Ni(Fe,Al)$_2$O$_4$ FILMS

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ABSTRACT

Preliminary results are reported about the growth of single crystal Ni(Fe,Al)$_2$O$_4$ films, grown by means of liquid phase epitaxy on (111)MgO and on (111)ZnGa$_2$O$_4$ substrates using a PbO-B$_2$O$_3$-Fe$_2$O$_3$ solvent. While films grown upon MgO show stress relief at the growth temperature, films grown upon ZnGa$_2$O$_4$ possess a tensile strain due to elastic deformation. Since $\lambda_{111}$ for NiFe$_2$O$_4$ is strongly negative a stress-induced uniaxial anisotropy is present in the films. Stripe domains can be observed with the Bitter technique and when a magnetic field is applied perpendicular to the plane of the film, magnetic bubbles with a diameter of ~2 μm appear. A bubble stability factor $q$ exceeding unity is obtained. For the first time magnetic bubbles are found in LPE grown spinel ferrites.

Introduction

Single crystalline oxidic bubble materials found and studied so far are orthoferrites, hexagonal ferrites, garnets and spinel ferrites. The applicability of the orthoferrites has found its limitations in the too large bubble diameters (1). The possibilities of the hexagonal ferrites have not been studied extensively but extremely low bubble mobilities have been reported so far (2). While the orthoferrites and the hexagonal ferrites are materials possessing a uniaxial anisotropy due to their crystal symmetry the garnets and spinels are intrinsically cubic with four equivalent (111) magnetic axes. The presence of growth-induced anisotropy in the garnets however, together with stress-induced anisotropy due to the lattice mismatch gives a uniaxial magnetic material suitable for magnetic bubble applications.

Probably caused by the success of the garnets no extensive studies have been made of the spinel ferrites in this regard, although growth-induced anisotropies are reported for flux grown spinel ferrites (3). Recently films of good quality have been grown by CVD (4-6) and LPE (7-9) procedures. Spinel ferrite films supporting magnetic bubbles have so far only been grown by CVD methods. Preliminary experiments indicate that at least a stress induced anisotropy can be generated in LPE grown NiFe$_{2-x}$Al$_x$O$_4$ films on (111)ZnGa$_2$O$_4$ substrates resulting in an easy axis of...
magnetization perpendicular to the plane of the film. Stripe domains and cylindrical domains (bubbles) can be observed.

**Theory**

For the existence of stable isolated bubble domains a unique axis of magnetization perpendicular to the plane of the film must be realized in such a way that the stability factor \( q \) is greater than unity. \( q = K_u / 2\pi M_s^2 \), where \( K_u \) is the uniaxial anisotropy constant and \( M_s \) the saturation magnetization. In order to achieve this, the use of low moment spinel ferrites is favourable. Low \( 4\pi M_s \) values can be obtained when a part of the Fe ions is substituted by Al ions. The existence of a compensation point in the \( 4\pi M_s \)-composition diagram is very helpful (as with the garnets) in this regard; low moment materials with relatively high Curie temperatures are obtained when few Fe ions are substituted by Al ions. Compensation points are known in several spinel systems e.g. \( \text{NiFe}_2-x\text{Al}_x\text{O}_4 \), \( \text{NiFe}_2-x\text{V}_x\text{O}_4 \) and \( \text{Li}_{0.5}\text{Fe}_{2.5-x}\text{Al}_x\text{O}_4 \). In Table I the room temperature compensation points together with the Curie temperatures and lattice constants are given.

In this study we have paid attention to the \( \text{NiFe}_2-x\text{Al}_x\text{O}_4 \) system. \( \text{NiFe}_2\text{O}_4 \) is an inverse spinel: \( \text{Fe}[\text{NiFe}]\text{O}_4 \). When part of the Fe ions are substituted by Al ions, this substitution is predominantly made on octahedral sites (13). For \( x = 0.7 \) the cation distribution can be written as \( \text{Fe}_{0.9}\text{Al}_{0.1}[\text{NiFe}_{0.4}\text{Al}_{0.6}]\text{O}_4 \).

The uniaxial anisotropy can be both stress and growth induced. The stress-induced anisotropy of a (111) film can be calculated from the magnetostriction constant \( \lambda_{111} \) and the stress \( \sigma \) in the film according to \( K_u = -3/2\lambda_{111} \sigma \). Besser c.s. (14) have developed a stress model for heteroepitaxial magnetic oxide films: For small misfit values the stress is caused by elastic deformation of the film at the deposition temperature resulting in a stress:

\[
\sigma = \frac{E}{1-\nu} \frac{a_s - a_f}{a_f}
\]

\( E \) is Young's modulus, \( \nu \) the Poisson constant, \( a_s \) the substrate lattice parameter and \( a_f \) the unstrained film lattice parameter. For higher misfit values at the deposition temperature the stress is probably relieved by the formation of misfit dislocations at the substrate-film interface (15) resulting in a bulk lattice constant of the film. The stress of the film at room temperature then results from the differences in expansion coefficients of

| Room temperature compensation points of spinel ferrite systems together with Curie temperatures \( \theta_c \) and lattice constants. |
|---|---|---|
| system | \( x \) | \( \theta_c \) (°C) | \( a_0 \) (Å) | Ref. |
| \( \text{NiFe}_2-x\text{Al}_x\text{O}_4 \) | 0.68 | 300 | 8.23 | (10) |
| \( \text{NiFe}_2-x\text{Rh}_x\text{O}_4 \) | 0.60 | 400 | 8.36 | (11) |
| \( \text{NiFe}_2-x\text{V}_x\text{O}_4 \) | 0.70 | 400 | 8.34 | (11) |
| \( \text{Li}_{0.5}\text{Fe}_{2.5-x}\text{Al}_x\text{O}_4 \) | 0.70 | 350 | 8.26 | (12) |
| \( \text{Li}_{0.5}\text{Fe}_{2.5-x}\text{Rh}_x\text{O}_4 \) | 0.80 | 50 | 8.40 | (11) |
film \( \sigma_f \) and substrate \( \sigma_s \) and from the temperature difference \( \Delta T \) between deposition temperature and room temperature giving

\[
\sigma_2 = \frac{E}{1 - v} (\sigma_f - \sigma_s) \Delta T.
\]

In the case of NiFe\(_2\)O\(_4\) deposited on MgO substrates the films are predicted to be in tension \( \sigma_f > 0 \) when elastic deformation occurs and in compression \( \sigma_f < 0 \) when stress relief occurs at the growth temperature. When only elastic deformation occurs the stress-induced uniaxial anisotropy for (111) films can be written as:

\[
K_s = -3/2 \lambda_{111} \frac{E}{1 - v} \frac{\sigma_s - \sigma_f}{\sigma_f}
\]

For NiFe\(_2\)O\(_4\) \( \lambda_{111} = 21 \times 10^{-6} \) (16), while for Ni\(_0.8\)Fe\(_{2.2}\)O\(_4\) \( \lambda_{111} = -4 \times 10^{-6} \) (17). This means that nickelferrite films grown in tension on (111) substrates will have a positive stress-induced anisotropy. For example NiFe\(_2\)O\(_4\) with a first order anisotropy constant \( K_1 \) of \( -0.7 \times 10^5 \) erg/cm\(^3\) gives a \( K_s \) value of about \( +6.5 \times 10^5 \) erg/cm\(^3\) while the demagnetization energy \( 2\pi M_s^2 \) is about \( 4.5 \times 10^5 \) erg/cm\(^3\). Here we have assumed \( E = 1.6 \times 10^{12} \) dyn/cm\(^2\) and \( v = 0.3 \) (18). In view of this consideration one may expect stable bubbles in NiFe\(_{2-x}\)Al\(_x\)O\(_4\) film, assuming that stress relief can be suppressed.

**Experimental**

LPE growth of NiFe\(_{2-x}\)Al\(_x\)O\(_4\) layers is performed according to standard LPE procedures described previously (8). The vertical way of dipping was used without substrate rotation. MgO with \( 2a_0 = 8.42 \) Å and ZnGa\(_2\)O\(_4\) with \( a_0 = 8.33 \) Å are used as substrates. The (111) MgO wafers were cut from a boule of MgO within 0.5° of the desired plane and afterwards ground with SiC and polished with syton. The ZnGa\(_2\)O\(_4\) substrates were grown from a Pb\(_2\)P\(_2\)O\(_7\) flux (19) and were used in the as-grown state having \{111\} facets measuring about 5-6 mm along the edge.

The flux is based on PbO, B\(_2\)O\(_3\), NiO, Fe\(_2\)O\(_3\) and Al\(_2\)O\(_3\) all reagent grade. The flux composition for the growth of pure NiFe\(_2\)O\(_4\) is nearly identical to the one used by Robertson (7) for the LPE growth of NiFe\(_2\)O\(_4\). The NiO content is much lower however than used by Rybal'skaya in his solubility study (20). The saturation temperature of the melt is strongly dependent on the NiO and B\(_2\)O\(_3\) contents which can be varied over wide ranges. The melt compositions used by Robertson and by Rybal'skaya and the compositions used in this study are collected in table II.

The saturation temperatures of the melts were not actually determined. A temperature indication was found by observing the surface of the melt when the temperature was lowered at a rate of about 2°C/min after stirring at elevated temperatures. When crystals were observed floating on the surface of the melt the corresponding temperature \( T_c \) was taken as the lowest temperature at which LPE growth was to be performed. The actual growth temperatures were chosen between \( T_c \) and \( T_c + 40^\circ\)C. The deposition times were varied between 5 and 10 minutes resulting in film thicknesses from about 1 μm to over 10 μm.

The lattice constants of the spinel ferrite films were determined by X-ray diffraction by measuring the Bragg’s angle from planes parallel to (111) using the substrate as internal standard. The compositions of the films were calculated from electron
Table II

Melt compositions used by Robertson (7) and Rybal'skaya (20) and the compositions used in this study, together with the observed $T_c$ values (consult text). Compositions normalized to 250 g PbO.

<table>
<thead>
<tr>
<th>Melt</th>
<th>PbO</th>
<th>$B_2O_3$</th>
<th>$Fe_2O_3$</th>
<th>$Al_2O_3$</th>
<th>NiO</th>
<th>$T_c$(°C)</th>
</tr>
</thead>
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<tr>
<td>Robertson</td>
<td>250</td>
<td>8.33</td>
<td>18.58</td>
<td>-</td>
<td>0.87</td>
<td>-</td>
</tr>
<tr>
<td>Rybal'skaya</td>
<td>250</td>
<td>5.26</td>
<td>18.21</td>
<td>-</td>
<td>8.51</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>250</td>
<td>10</td>
<td>17</td>
<td>-</td>
<td>1</td>
<td>930</td>
</tr>
<tr>
<td>B</td>
<td>250</td>
<td>10</td>
<td>17</td>
<td>1</td>
<td>1</td>
<td>940</td>
</tr>
<tr>
<td>C</td>
<td>250</td>
<td>10</td>
<td>17</td>
<td>3</td>
<td>1</td>
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<td>15</td>
<td>17</td>
<td>5</td>
<td>1</td>
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</tr>
<tr>
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<td>15</td>
<td>17</td>
<td>6</td>
<td>1</td>
<td>995</td>
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<tr>
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<td>17</td>
<td>6</td>
<td>1</td>
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<tr>
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<td>30</td>
<td>17</td>
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<td>1</td>
<td>855</td>
</tr>
<tr>
<td>I</td>
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<td>35</td>
<td>17</td>
<td>6</td>
<td>1</td>
<td>830</td>
</tr>
</tbody>
</table>

Microprobe data using NiFe$_{2-x}$Al$_x$O$_4$ standards with $x = 0, 0.5$ and $1.0$. The accuracy appeared to be better than 0.02 atoms per formula unit.

Since NiFe$_2$O$_4$ is not transparent to visible light domain structures were investigated with the aid of the Bitter technique. A magnetic field reaching up to 1000 Oe could be applied perpendicular to the plane of the film using an electromagnet.

Results and discussion

Film parameters

All films were shown to be pure spinels with a Ni content of $0.99 \pm 0.02$ atoms per formula unit. Films grown upon MgO substrates exhibit more cracks than films grown upon ZnGa$_2$O$_4$ substrates. When the Al content of the films increases, cracking becomes more severe. When a high supersaturation is used during the growth, spiral growth and growth hillocks can be observed (Fig. 1). By raising the Al content of the melt (compositions A-E) the Al content of the film increases. The saturation temperature can be decreased considerably by adding $B_2O_3$ to the melt. This results in a decrease of the Al content of the films, as is shown for compositions E-I in Fig. 2. (also cf. Table II). The Pb content of the film decreases with increasing growth temperature from 0.02 atoms Pb per formula unit at 840°C to less than 0.005 atoms Pb at 1020°C.

When the Al content of the films is plotted versus the strained film lattice constants as in Fig. 3, all points are close to a straight line resembling Vegard's relationship between unstrained (bulk) lattice constants and Al contents in NiFe$_{2-x}$Al$_x$O$_4$ as reported by Schulkes c.s. (12). These bulk values were confirmed by our own measurements.

Because there are distinct deviations from Vegard's relation depending both on the type of substrate used and on the Al content of the film, we will compare our data with calculated values assuming either 100% elastic deformation or 100% stress relief at the deposition temperature.

Using a Poisson constant of 0.3 for the NiFe$_{2-x}$Al$_x$O$_4$ system
and $x = 0.6 \ (a_0 = 8.249 \ \text{Å})$ the strained lattice constant, assuming 100% elastic deformation, would be 8.08 Å on MgO and 8.18 Å on ZnGa$_2$O$_4$ substrates. The connection between the strained lattice constants and the Al content is drawn in Fig. 3 for MgO and ZnGa$_2$O$_4$ substrates.

When stress relief occurs at the growth temperature the resulting room temperature stress $\sigma_2$ can be calculated from the known expansion coefficients for MgO (8), NiFe$_2$O$_4$ (17) and ZnGa$_2$O$_4$ (18) of respectively $1.34 \times 10^{-5}$, $1.00 \times 10^{-5}$ and $0.95 \times 10^{-5}$ °C$^{-1}$ (20-900°C). Films grown upon MgO will be in compression while films grown upon ZnGa$_2$O$_4$ will be in tension. If one assumes that in the stress relieved film elastic deformation occurs during cooling to room temperature the strained lattice constants can be calculated. Using a $\Delta T$ of 900°C ($a_s - a_f$) for MgO substrates is $-0.047 \ \text{Å}$ and $+0.007 \ \text{Å}$ for ZnGa$_2$O$_4$ substrates.

Now from Fig. 3 it can be concluded that in the case of MgO substrates stress relief occurs at the growth temperature. The measured values for ($a_s - a_f$) are about $-0.01 \ \text{Å}$, compared to $-0.047$ theoretically. Obviously some strain is released by cracking of the film. In the case of ZnGa$_2$O$_4$ substrates our data are consistent with the values calculated assuming 100% elastic deformation up to $x = 0.16$ in NiFe$_{2-x}$Al$_x$O$_4$. This corresponds with a room temperature mismatch of 0.02 Å in tension. For greater misfit values ($x > 0.16$) stress relief occurs at the deposition temperature and film cracking is also observed which explains the fact that our data are a little higher than according to a 100% stress relief model. The films grown upon ZnGa$_2$O$_4$ with $x = 0.78$ and 0.94 are grown at relatively high temperature and as a consequence interdiffusion between film and substrate can occur resulting in a higher film lattice constant. (The occurrence of interdiffusion can be shown by annealing a NiFe$_2$O$_4$ film on a MgO substrate at 1100°C: A solid solution of NiFe$_2$O$_4$ and MgFe$_2$O$_4$ is formed with a higher lattice constant than pure NiFe$_2$O$_4$).
Domain structure

As expected from the stress considerations no domain structure could be made visible on films grown upon (111) MgO substrates. Whereas pure NiFe$_2$O$_4$ deposited upon ZnGa$_2$O$_4$ showed a pattern typically caused by the first order crystal anisotropy (Fig. 4), Al-substituted Ni-ferrite films grown in tension upon (111) ZnGa$_2$O$_4$ substrates exhibit stripe domains resembling the patterns observed on uniaxial garnet films. The best developed patterns are found for NiFe$_{2-x}$Al$_x$O$_4$ films with $x = 0.11$ and 0.16; films which are elastically deformed. Films with $x = 0.26$ and $x = 0.44$ also show sharp stripe domains but not over the entire surface; in the neighbourhood of cracks the structure disappears. The strip period ranges from 1.6 μm for $x = 0.11$ to 2.3 μm for $x = 0.44$. Films with higher Al contents show more diffuse domain patterns. When a magnetic field is applied perpendicular to the plane of the film the strip width increases with increasing field. Stripe domains occurring in films with $x = 0.61$ (Fig. 5) and $x = 0.78$ can be contracted to cylindrical domains. For $x = 0.61$ bubbles with a diameter of ~2 μm appear at about 550 Oe biasfield and when this field is increased further to about 600 Oe the bubbles contract to about 75% of their original diameter and collapse. For the film with $x = 0.78$ these values are respectively 350 and 400 Oe. Bubble observations in the films with $x < 0.44$ (Fig. 6) could not be made. With a biasfield larger than 600 Oe the half domain period becomes too small and the domain boundary becomes too diffuse to follow further contraction.

In Fig. 7 we have plotted the Al content of NiFe$_{2-x}$Al$_x$O$_4$ versus calculated values of $2M_S$, $K_{uE}$ (ED) (due to elastic deformation) and $K_{uS}$ (SR) (assuming

FIG. 3.
Al content versus the strained lattice constants of NiFe$_{2-x}$Al$_x$O$_4$ films grown on (111) MgO (o) or (111) ZnGa$_2$O$_4$ (○). Also the measured unstrained lattice constants (x) are plotted. Solid line represent Vegard's relationship, whereas the dashed-dotted line and dashed line represent calculated values of strained lattice constants for respectively films on MgO and on ZnGa$_2$O$_4$ assuming 100% elastic deformation.

FIG. 4.
Domain pattern observed on a (111) NiFe$_2$O$_4$ film grown on ZnGa$_2$O$_4$. The film exhibits a small compressive strain (0.003 Å in compression).
stress relief at the deposition temperature and subsequent elas-
tic deformation during cooling). The values of $K_s$ are calculated
using the value of $\lambda_{111}$ for $x = 0$. Up to $x = 0.16$ $K_s$ (ED) is va-
lid and a stability factor $q$ of 0.54 is found for $x = 0.16$. For
$x > 0.44$ at which stress relief occurs at the growth temperature,
we calculate from $K_s$ (SR) a value of $q = 1.7$ for $x = 0.44$ and
about 7 for $x = 0.61$, but an uncertainty due to the fact that
$\lambda_{111} = f(x)$ must be kept in mind.

The occurrence of stress relief in films grown on MgO may
also have consequences for the interpretation of our results on
CuFe$_2$O$_4$ films reported in ref. (9). The reported calculated va-
lues of the stress-induced anisotropy constants might be in error
since we did not account for stress relief.

Conclusions

We have shown that stoichiometric NiFe$_{2-}\!_x$Al$_x$O$_4$ films can be
deposited on (111) MgO and on (111) ZnGa$_2$O$_4$ substrates. Films
grown upon MgO are suffering from severe stress relief and as a
consequence MgO substrates are entirely unsuitable for growth of
Al-substituted nickel ferrite films with bubble applications.
Films grown upon ZnGa$_2$O$_4$ are much better in this regard; up to
0.02 Å in tension elastic deformation occurs. Films grown in ten-
sion with $\lambda_{111} < 0$ have a uniaxial anisotropy perpendicular to
the plane of the film. Due to the existence of a compensation
point low-moment films can be grown with a stability factor ex-
ceeding unity. Stripe domains can be observed with the Bitter
technique. By applying a magnetic field perpendicular to the
plane of the film magnetic bubbles can be generated.

Since the results obtained so far are very encouraging the
work on the nickel ferrite system is elaborated further. On
Zn(Ga,Al)$_2$O$_4$ substrates with lattice constants ranging from 8.28-
8.23 Å it should be possible to deposit elastically deformed
NiFe$_{2-}\!_x$Al$_x$O$_4$ films with a bubble stability factor $q$ reaching up
to 5 or even higher.

The deposition process itself can certainly be improved: By
lowering the NiO content or by increasing the B$_2$O$_3$ content of the
flux the saturation temperature can be decreased considerably.
Film growth at lower temperatures is less influenced by differences
in expansion coefficients of film and substrate. Also pro-
blems arising from interdiffusion between substrate and film are

![FIG. 5.](image)

Domain pattern observed on a NiFe$_{2-}\!_x$Al$_x$O$_4$ film with $x = 0.61$
grown on (111) ZnGa$_2$O$_4$. A magnetic field is present perpendicular
to the plane of the film a) 0 Oe, b) 250 Oe, c) 500 Oe, d) 560 Oe
and e) 590 Oe.
eliminated when low temperatures can be used.

Knowledge of the expansion coefficients of film and substrate and knowledge of the magnetostriction constants of the NiFe$_{2-x}$Al$_x$O$_4$ series are essential in order to calculate the stress-induced anisotropy.

FIG. 6.
Domain pattern observed on a NiFe$_{2-x}$Al$_x$O$_4$ film with $x = 0.44$ grown on (111) ZnGa$_2$O$_4$. A magnetic field is present perpendicular to the plane of the film: a) 0 Oe, b) 250 Oe and c) 500 Oe.

FIG. 7.
$2\pi M_s^2(10)$ and $K^S$ versus the Al content of NiFe$_{2-x}$Al$_x$O$_4$ films. $K^S$ (ED): calculated assuming 100% elastic deformation. $K^S$ (SR): calculated assuming 100% stress relief. Calculations are performed using $\lambda_{111}$ for pure NiFe$_2$O$_4$ for all compositions.
References