

LPE growth and magnetic anisotropy of Ni(Fe,Al)2O4 films

Citation for published version (APA):

Straten, van der, P. J. M., Bondarenko, V. V., & Metselaar, R. (1981). LPE growth and magnetic anisotropy of Ni(Fe,Al)2O4 films. *Journal of Crystal Growth*, 51(1), 119-130. [https://doi.org/10.1016/0022-0248\(81\)90016-6](https://doi.org/10.1016/0022-0248(81)90016-6)

DOI:

[10.1016/0022-0248\(81\)90016-6](https://doi.org/10.1016/0022-0248(81)90016-6)

Document status and date:

Published: 01/01/1981

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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LPE GROWTH AND MAGNETIC ANISOTROPY OF Ni(Fe, Al)₂O₄ FILMS

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Received 10 April 1980

Results are reported about the LPE growth of Ni(Fe,Al)₂O₄ films grown onto (100), (110) and (111) MgO and on (111) ZnGa₂O₄, Zn(Ga,Al)₂O₄ and Zn(Ga,Fe)₂O₄ substrates using a PbO–B₂O₃ flux. For small film thicknesses and small lattice mismatches elastically deformed films, showing no stress relief, can be grown on the spinel substrates. Interdiffusion between film and substrate occurs to a small extent when spinel substrates are used. For films grown in tension, positive uniaxial anisotropies are found and stripe domains are observed at the film surface. It is shown that the anisotropy can be explained by the stress in the film and the negative magnetostriction constant of NiFe_{2–x}Al_xO₄. Crack-free films with a uniaxial anisotropy energy exceeding the demagnetization energy are obtained when the misfit is lower than 0.03 Å and 0.50 < x < 0.65. For those films the stripe domains can be contracted to bubbles with the use of a bias field.

1. Introduction

A stress-induced anisotropy K_u^s is present in spinel epitaxial films when a stress σ is present in the spinel film at room temperature. When λ is the magnetostriction constant of the film, the stress-induced anisotropy can be calculated as

$$K_u^s = -\frac{3}{2}\lambda_{111}\sigma, \quad (1)$$

for films grown on (111) substrates. The stress σ at room temperature [1] can be calculated as

$$\sigma = \left[(1 - \eta) \frac{a_s - a_f}{a_f} + \eta(\alpha_f - \alpha_s) \Delta T \right] \frac{E}{1 - \nu}, \quad (2)$$

where a_s , a_f = bulk room temperature lattice parameters of substrate and film respectively, α_s , α_f = thermal expansion coefficients of substrate and film respectively, ΔT = difference between deposition temperature and room temperature, E = Young's modulus, ν = Poisson ratio, and η = fractional stress-relief ($0 \leq \eta \leq 1$).

For small misfit ($a_s - a_f$) values and thin films, the

film is strained elastically to bring the lattices of film and substrate into register at the interface ($\eta = 0$). For higher misfit values and thicker films it is assumed that the film takes on its equilibrium free lattice constant away from the interface, so that it is essentially unstressed at the deposition temperature. The misfit stress is relieved by the formation of misfit dislocations. Since the strain energy increases with increasing film thickness, there is a critical thickness, h_c , above which it becomes energetically favourable to form misfit dislocations [2]:

$$h_c = \frac{b(1 + \nu)a_f}{8\pi(a_s - a_f)} [\ln(r/b) + 1], \quad (3)$$

where b is the Burgers vector and r the dislocation strain-field radius. When stress relief occurs at the deposition temperature ($\eta = 1$) and when the film is considered to behave elastically on cooling to room temperature, a stress develops due to differences between α_f and α_s . Intermediate situations ($0 < \eta < 1$) are also possible.

In a previous article [3] a stress-induced anisotropy was reported in LPE grown Ni(Fe,Al)₂O₄ films. On films, grown in tension ($a_s > a_f$) upon ZnGa₂O₄ substrates, a serpentine-like domain pattern could be made visible with Bitter fluid. Since for these films $\sigma > 0$ and $\lambda_{111} < 0$, a positive stress-

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induced anisotropy results. In this article we report about the growth and characterization of Ni(Fe,Al)₂O₄ films grown upon MgO, ZnGa₂O₄, Zn(Ga,Al)₂O₄ and Zn(Ga,Fe)₂O₄ substrates.

2. The growth of Al- and Fe-substituted zinc gallate substrates

In order to grow compressively and tensively stressed Ni(Fe,Al)₂O₄ films, substrates are needed with different lattice constants. The substrates are based on ZnGa₂O₄ ($a_0 = 8.336 \text{ \AA}$) which can be grown from a ZnO–Ga₂O₃–Pb₂P₂O₇ melt by slow cooling [4]. Octahedrally shaped crystals with {111} facets of dimensions up to 6 mm along the edge could be obtained. When Al₂O₃ or Fe₂O₃ is added to the melt, doped zinc gallates are obtained with lattice constants respectively lower and higher than 8.336 Å. (Table 1). The lattice constants of the crystals were determined by X-ray diffractometry by measuring the Bragg angles from planes parallel to the (111) facet face. Since from ceramic standards a linear relation was found between composition and lattice constants in the Al- and Fe-substituted ZnGa₂O₄ systems, the composition near the surface of the crystals could be determined from the lattice constants. Although the surface compositions of crystals obtained from one melt composition are rather close to each other, we always find some composition range. Concentration gradients in the melt during the growth or slightly different growth rates must be the cause of this. When the surface compositions of the crystals are compared with the melt composition, we find for Fe

a 60% higher and for Al a 40% lower concentration (fig. 1). Also at the growth of Ni(Fe,Al)₂O₄ single crystals [5] a lower concentration of Al was found. The effect was more pronounced with a Pb₂P₂O₇ flux (–50%) than with a PbO–B₂O₃ flux (–30%).

We have performed microprobe analyses on crystals cut through the centre. Up to about 1 mm from the surface, the composition remained rather constant and was in excellent agreement with the composition determined from the lattice constant of the crystal. However, more towards the centre of the crystals a distinct concentration gradient was found. For the Zn(Ga,Fe)₂O₄ crystals the Fe content decreases towards the centre, while for the Zn(Ga, Al)₂O₄ crystals the Al content increases. In a large ZnGa_{2–x}Fe_xO₄ crystal (7 mm) grown from a melt corresponding with $x = 0.38$ we find a value of $x = 0.60$ near the surface and a value of $x = 0.31$ in the centre.

The concentration gradients in the crystals must be due to a strong temperature dependence of the segregation coefficients for Fe and Al, defined as the molar ratios:

$$k_M = [M/(M + Ga)]_{\text{crystal}} / [M/(M + Ga)]_{\text{melt}}, \quad (4)$$

where M = Fe or Al respectively.

Since the crystals are grown from the melt by slow cooling with a rate of approximately 1°C/h from 1300–800°C, the material in the centre of the largest crystals will be grown at high temperatures, while the outer part of the large crystals and the entire small crystals are grown at lower temperatures. In the high temperature region $k_{\text{Al}} > 1$ and $k_{\text{Fe}} < 1$; the reverse will be true in the low temperature region.

Table 1

Melt composition (moles) for the flux growth of ZnGa_{2–x}Fe_xO₄ and ZnGa_{2–x}Al_xO₄ single crystals and surface lattice constants of the crystals a_s

x	Pb ₂ P ₂ O ₇	ZnO	Ga ₂ O ₃	Fe ₂ O ₃	Al ₂ O ₃	a_s (Å)
0	0.40	0.48	0.120	–	–	8.336
0.20	0.40	0.48	0.108	0.012	–	8.348–8.351
0.38	0.40	0.48	0.097	0.023	–	8.360–8.367
0.76	0.40	0.48	0.074	0.046	–	8.392–8.397
0.35	0.40	0.48	0.099	–	0.021	8.310–8.300
0.70	0.40	0.48	0.078	–	0.042	8.286–8.270

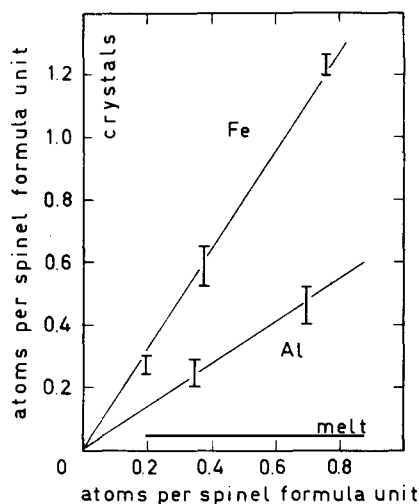


Fig. 1. Surface compositions of Zn(Ga, Fe)₂O₄ and Zn(Ga, Al)₂O₄ crystals versus the compositions calculated from the Ga/Fe and Al/Fe ratios in the melts.

The presence of concentration gradients in the crystals is not serious when the crystals are used as substrates in LPE spinel growth, since the composition at the surface of a crystal is constant. The misfit between film and substrate is dictated by the difference between film lattice constant and surface lattice constant of the substrate.

3. The growth of Ni(Fe, Al)₂O₄ films

For the LPE growth we have used a melt composed of 1 PbO, 0.13 B₂O₃, 0.013 NiO and 0.11 Fe₂O₃ (moles) for the growth of pure NiFe₂O₄ films. For the growth of Al-substituted films 0.05 moles Al₂O₃ were added to the melt per mole PbO and the B₂O₃ content ranged from 0.13 to 0.45 moles B₂O₃ per mole PbO. The flux constituents were mixed and premelted in a 75 ml Pt crucible; the total load was about 300 g. Actually 1 wt% of the PbO was replaced by PbO₂ for protection of the crucible. The crucible was placed in a vertical three-zone resistance furnace having a large isothermal area. The film growth is performed by dipping a substrate for a certain time in the supersaturated melt at a constant temperature. Afterwards, the substrate-film combination is cleaned in a hot dilute acetic-nitric acid solution.

When spinel substrates are used, the films are grown directly on the (111) facets of the substrates with no other precautions than cleaning of the substrates. MgO substrates are cut from a boule of MgO using an internal diamond cutting blade. Substrates having (100), (110) and (111) orientations, cut within 0.5°, were used. Cutting damage was removed by polishing with SiC and syton.

The LPE grown Ni(Fe,Al)₂O₄ films are characterized using three parameters: the Al content, the thickness and the lattice constant difference between film and substrate (misfit).

From microprobe data all films were shown to be pure spinels with a Ni content of 0.99 ± 0.02 atoms Ni and a Pb content less than 0.02 atoms Pb per spinel formula unit. When the PbO, B₂O₃ and NiO content of the melt is kept constant, the Al content in the films increases when the Al₂O₃ : Fe₂O₃ ratio in the melt is increased. When the B₂O₃ content in the melt is increased, keeping the other components constant, the saturation temperature of the melt and the Al content in the film decrease. In fig. 2 the relation between the Al content of the film and the B₂O₃ content in the melt is plotted. Saturation temperatures are determined by extrapolating to zero growth rate. Undercoolings up to 60°C are used. When the melt composition is kept constant, the Al content in the film increases by about 10% when decreasing the undercooling from 60 to 10°C.

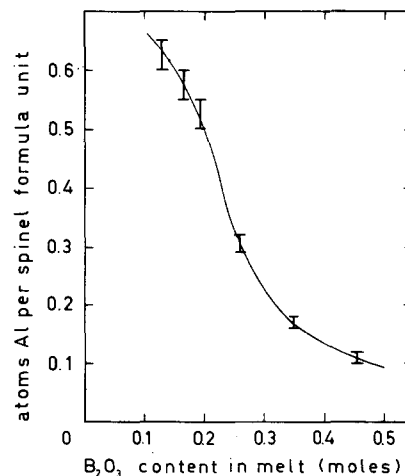


Fig. 2. Aluminum content in Ni(Fe,Al)₂O₄ films versus the amount of B₂O₃ (moles) in the melt per mole PbO. Undercooling during the growth of the films between 10 and 60°C.

The film thickness can in principle be determined by grinding a steel sphere, coated with diamond paste, through the film. This method, however, can only be applied successfully when the film thickness is reasonably constant over the substrate surface. Films grown on (100) and (110) MgO were rough with surfaces consisting respectively of pyramids and ridges composed of (111) facets. Films grown on (111) MgO substrates are reasonably flat, but due to the slight misorientation ($<0.5^\circ$) of the substrates, small terraces can be observed on the surface of the films. Obviously, only LPE growth on the habit face (111) results in a smooth surface. For films on MgO substrates the film thickness could be determined within 10%.

When films are grown on the natural (111) facets of flux grown spinel substrates, hillocks are observed on the film surfaces with heights up to $4\ \mu\text{m}$ and base cross sections up to $200\ \mu\text{m}$. The hillocks are observed over the entire undercooling range used ($10\text{--}60^\circ\text{C}$). Since for spinels (111) is a habit face, growth may occur by two-dimensional nucleation or by a spiral growth mechanism. The hillocks grow by means of the spiral growth mechanism, in which a screw dislocation, with its Burgers vector ending on the surface, acts as a continuous step source. In literature, growth hillocks are reported in (111) spinel [6] and (110) garnet [7,8] films, orientations corresponding to habit faces of spinel and garnet respectively. Since surface irregularities seem to act as step sources, the density of the hillocks, especially when low undercoolings are used, could be reduced by boiling the substrates for a short time in H_3PO_4 , but we did not succeed in removing them completely. Determination of the average film thickness is very inaccurate when large hillocks are present at the film surface. When the surface of the film is illuminated with thallium light ($\lambda = 0.54\ \mu\text{m}$), thickness variations are made visible. In figs. 3a–3c, thallium light photographs are shown for films grown from the same melt with the same dipping time, grown with increasing undercooling and as a consequence with increasing average film thickness. At the highest undercooling cracks can be observed, while at the lowest undercooling individual small hillocks are present.

The stress in the film results from the misfit between film and substrate, as described by eq. (2).

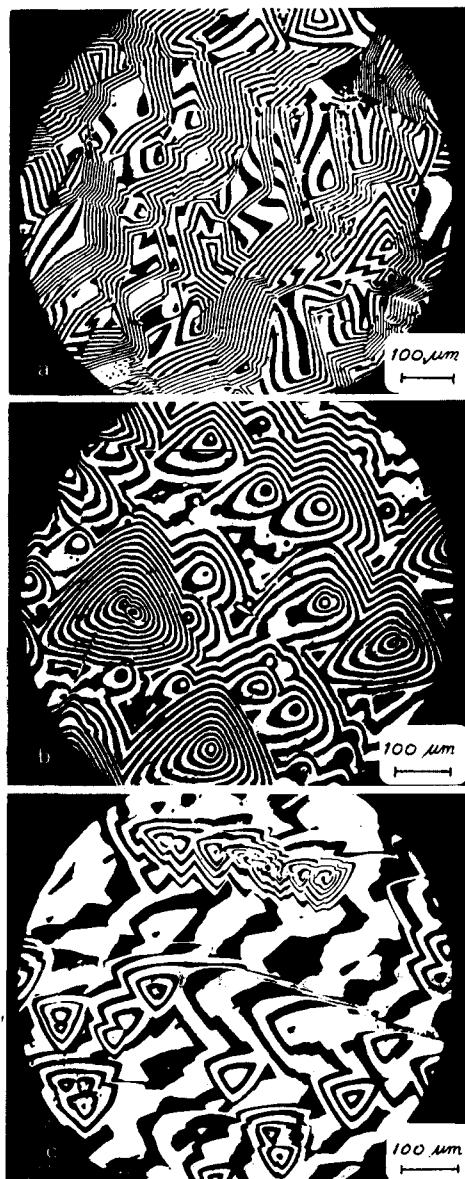


Fig. 3. Thickness variations in $\text{NiFe}_{2-x}\text{Al}_x\text{O}_4$ films with $0.16 < x < 0.18$, grown onto ZnGa_2O_4 substrates, observed by interferometry using thallium light ($\lambda = 0.54\ \text{\AA}$). Deposition time 10 min and growth temperature ($^\circ\text{C}$): (a) 928, (b) 947, (c) 975.

When the fractional stress relief η is zero, the growing film is deformed elastically and the substrate remains unchanged (substrate thickness \geq film thickness). The lattice constants are determined, using double crystal

X-ray diffractometry, from the Bragg angles of planes parallel to (111).

When a_f and a_s are the bulk room temperature lattice constants of film and substrate, respectively, and a_f^\perp is the measured lattice constant of the film on the substrate, determined from a film plane parallel to the film surface, it can be shown that for $\eta = 0$:

$$a_f^\perp - a_s = \frac{1 + \nu}{1 - \nu} (a_f - a_s). \quad (5)$$

Since for spinels the Poisson ratio is about 0.3, it follows that when $\eta = 0$, the measured misfit $\Delta a^\perp = 1.86 \Delta a$, in which Δa is the bulk misfit.

When 100% stress relief occurs at the deposition temperature ($\eta = 1$), a stress develops due to Δa and ΔT , which also causes a deformation of the spinel film. Using high temperature diffractometry, we have determined the thermal expansion coefficients for MgO, NiFe₂O₄, NiFe_{1.5}Al_{0.5}O₄, ZnGa₂O₄ and ZnGa_{1.5}Al_{0.5}O₄ (see table 2).

For the substrate-film combinations used in this study, $\alpha_f - \alpha_s$ is about $+0.05 \cdot 10^{-5} \text{C}^{-1}$ (spinel substrates) or about $-0.3 \cdot 10^{-5} \text{C}^{-1}$ (MgO substrates). With $\Delta T = 900^\circ\text{C}$ and $E = 1.6 \cdot 10^{12} \text{ dyn/cm}^2$ [9], a stress in the film of respectively $+0.1 \cdot 10^9$ and $-0.6 \cdot 10^9 \text{ N/m}^2$ is calculated ($\eta = 1$), resulting in a lower, respectively higher, value of a_f^\perp compared with a_f .

In conclusion: when the misfit is not too small, the state of stress can be followed, for a film with a fixed composition, grown upon a fixed substrate, by measuring a_f^\perp and knowing the values for $\eta = 0$ and $\eta = 1$.

In fig. 4 experimental and theoretical relations between a_s , a_f and a_f^\perp are presented, clearly showing the change of a_f^\perp with changing η .

Table 2

Thermal expansion coefficients for film and substrate materials (20–1000°C)

Compound	$\alpha \times 10^5 \text{ (}^\circ\text{C}^{-1}\text{)}$
MgO	1.30 ± 0.10
ZnGa ₂ O ₄	0.95 ± 0.05
ZnGa _{1.5} Al _{0.5} O ₄	0.90 ± 0.05
NiFe ₂ O ₄	1.00 ± 0.05
NiFe _{1.5} Al _{0.5} O ₄	0.95 ± 0.05

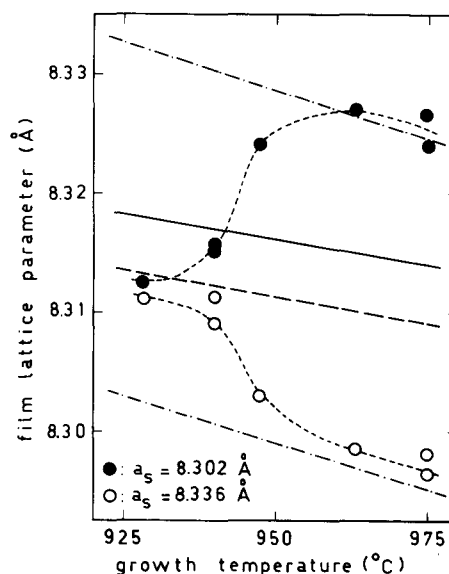


Fig. 4. Lattice parameters a_f^\perp for NiFe_{2-x}Al_xO₄ films with $0.16 \leq x \leq 0.18$ versus the growth temperature for films in tension (○) and in compression (●). Solid line indicates a_f , determined from the relation between composition and lattice parameter, dashed line $a_f^\perp(\eta = 1)$ and dash-dotted line $a_f^\perp(\eta = 0)$. The values of a_f^\perp are calculated from the stress in the film for the two extreme situations.

4. The domain structure of the films

When a stress is present in the film at room temperature, a uniaxial anisotropy energy results according to eq. (1). From magnetostriction measurements performed on NiFe_{2-x}Al_xO₄ single crystals (for $x = 0$ to 0.3) by means of laser interferometry [5,10], it is shown that λ_{111} is negative and $|\lambda_{111}|$ decreases with increasing Al content. For pure NiFe₂O₄, $\lambda_{111} = -22 \cdot 10^{-6}$ and from linear extrapolation it is found that λ_{111} approaches zero for $x \sim 0.8$. Knowing λ_{111} as a function of the Al content x in the film, we are able to calculate the stress-induced anisotropy energy K_u^s as a function of x for different misfit values assuming $\eta = 0$. The results are presented in fig. 5 with the lattice constant of the substrate as a parameter. From this figure it can be seen that when the misfit is high enough, the stress induced-anisotropy energy exceeds the demagnetization energy $2\pi M_s^2$ (M_s = saturation magnetization). With increasing Al content in the film, the minimum misfit

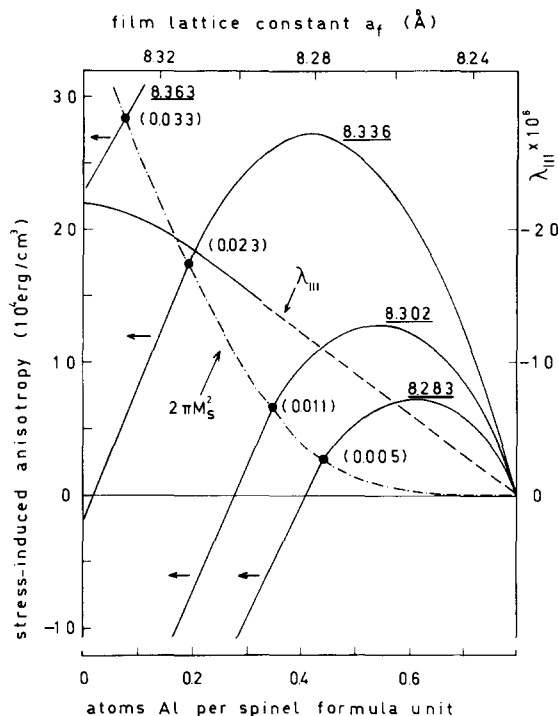


Fig. 5. Theoretical values for the stress induced anisotropy versus the aluminum content and the lattice parameter of Ni(Fe, Al)₂O₄ with the lattice parameter of the substrate as parameter (under-lined values in Å). Also the relation between λ_{111} and the aluminum content in Ni(Fe, Al)₂O₄ is given. The dashed parts of this relation are the values obtained by extrapolation. The values between brackets represent the misfits required to achieve $K_u^s > 2\pi M_s^2$.

required to achieve this situation decreases.

When Ni(Fe, Al)₂O₄ films are grown on MgO ($2a_0 = 8.42$ Å), no domain pattern could be observed. Obviously stress relief occurs at the deposition temperature due to the very large misfit and a compressive stress is present in the film at room temperature, resulting in a negative stress-induced anisotropy. On spinel substrates, however, where a closer lattice fitting is obtained, serpentine-like domain patterns are observed when films are grown in tension ($K_u^s > 0$), while for films grown in compression ($K_u^s < 0$) no domain pattern is observable anymore. When cracks are present in the film, the stress is relieved along the crack and the domain pattern vanishes (fig. 6). In all NiFe_{2-x}Al_xO₄ films with x ranging from zero up to 0.65, domain patterns are observed provided the films

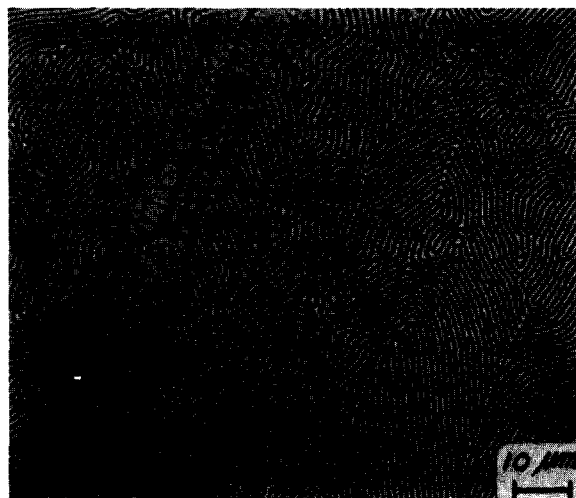


Fig. 6. Bitter domain pattern observed on a NiFe_{2-x}Al_xO₄ film with $x = 0.11$ grown onto a ZnGa₂O₄ substrate, showing the vanishing of the pattern near the crack.

were grown in tension and not too large misfit values were used ($\Delta a < 0.05$ Å). In general the width of the magnetic domains decreases with decreasing film thickness and with increasing saturation magnetization of the film (figs. 7a and 7b).

When a magnetic field is applied perpendicular to the plane of the film, the width of the domains with its magnetization in the same direction of the field increases, while the width of the other domains decreases with increasing field. When $0 < K_u < 2\pi M_s^2$, the domain pattern becomes diffuse and finally vanishes when the field is increased above a certain value. When $K_u > 2\pi M_s^2$, however, the domain pattern starts unwinding and the domains with their magnetization opposite to the direction of the field contract to cylindrical bubbles with increasing field. When the bias field is increased further, the bubble diameter decreases by about 25% and finally the bubble collapses (fig. 8). Given a certain film, the field at which the bubble collapses is not very well defined. When some serpentine like domains are still contracting towards bubbles, other domains are already in the bubble state, while some bubbles have already collapsed. Some bubbles only collapse when much higher field strengths are used. When, after complete saturation of the film, the magnetic field is reduced to zero, the serpentine-like domains

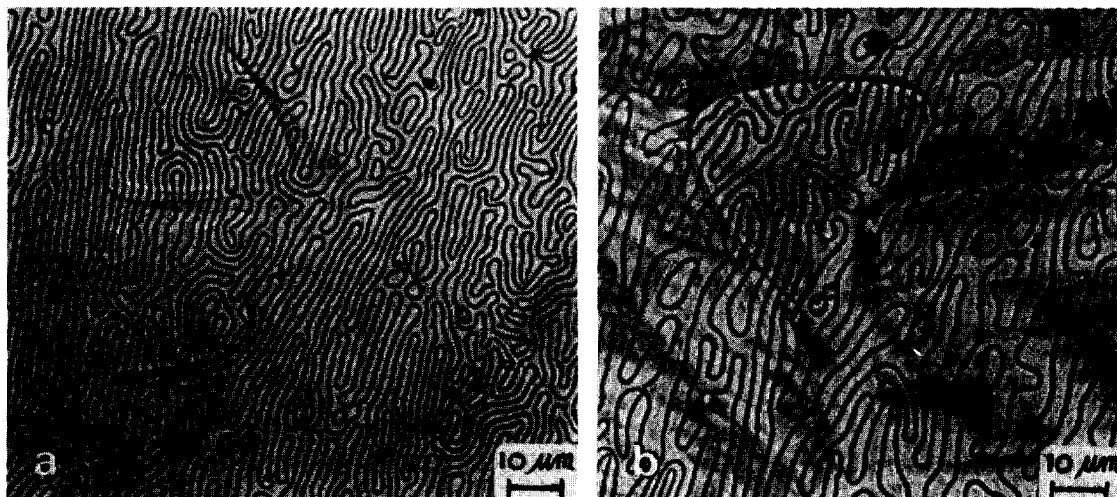


Fig. 7. Bitter domain patterns observed on NiFe_{2-x}Al_xO₄ films with $x = 0.58$ (7a) and $x = 0.63$ (7b) grown onto Zn(Ga,Al)₂O₄ substrates.

become visible again, but in some areas they are completely absent. When the film is demagnetized by heating for a short time above its Curie temperature or by moving a demagnetization pen over the film surface, the original domain pattern is obtained again. In general, crack-free NiFe_{2-x}Al_xO₄ films with $K_u > 2\pi M_s^2$ are obtained when $0.50 < x < 0.65$, and the films are grown in tension with a misfit lower than about 0.03 Å.

5. Anisotropy measurements

The uniaxial anisotropies in the Ni(Fe,Al)₂O₄ films are measured using a torque magnetometer. Therefore, after the growth of the films on the (111) facets of flux grown substrates, the crystals were shaped in such a way that one substrate facet with a film on one side was left.

The anisotropy is calculated as

$$K_u = \left(\frac{KV}{M_s V} \right) M_s + 2\pi M_s^2. \quad (6)$$

Theoretically eq. (6) also contains a contribution of the magnetocrystalline anisotropy K_1 [11]. This contribution, however, is very small and falls within the limits of inaccuracy.

KV is obtained from the torque measurement;

$M_s V$ is determined using a Faraday balance and M_s can be calculated when the volume of the film is known. For films grown on spinel substrates, however, inaccuracies up to 25% are present in the calculated M_s values caused by inaccuracies in the determination of the film thickness (growth hillocks). When the composition of the film is known, M_s can be taken from literature.

In calculating K_u from eq. (6), the small dimensions of our spinel substrates result in large inaccuracies. A 2 μm thick film, grown on a triangular facet measuring 5 mm along the edges, has a volume of about 2×10^{-5} cm³. When films are grown in tension with a misfit of 0.02 Å, KV ranges from about -2 erg for NiFe₂O₄ up to about +2 erg for NiFe_{1.4}Al_{0.6}O₄ films. The inaccuracy of the torque magnetometer is 2% for a 100 erg sample, but is 10% for a 10 erg sample. The lower limit is about 0.2 erg. Inaccuracies of 10–20% are to be expected.

For polycrystalline NiFe₂O₄, $M_s = 258$ Gauss according to Blasse and Gorter [12]. For polycrystalline NiFe₂O₄, sintered at 1250°C in oxygen, we obtained 265 ± 5 Gauss. For NiFe₂O₄ single crystals, however, grown from a PbO–B₂O₃ flux [5], a value of 229 ± 5 Gauss was obtained measured over more than 10 crystals. Since the PbO–B₂O₃ flux is strongly oxidizing, we believe that the higher M_s values found for polycrystalline samples are due to some Fe²⁺ in

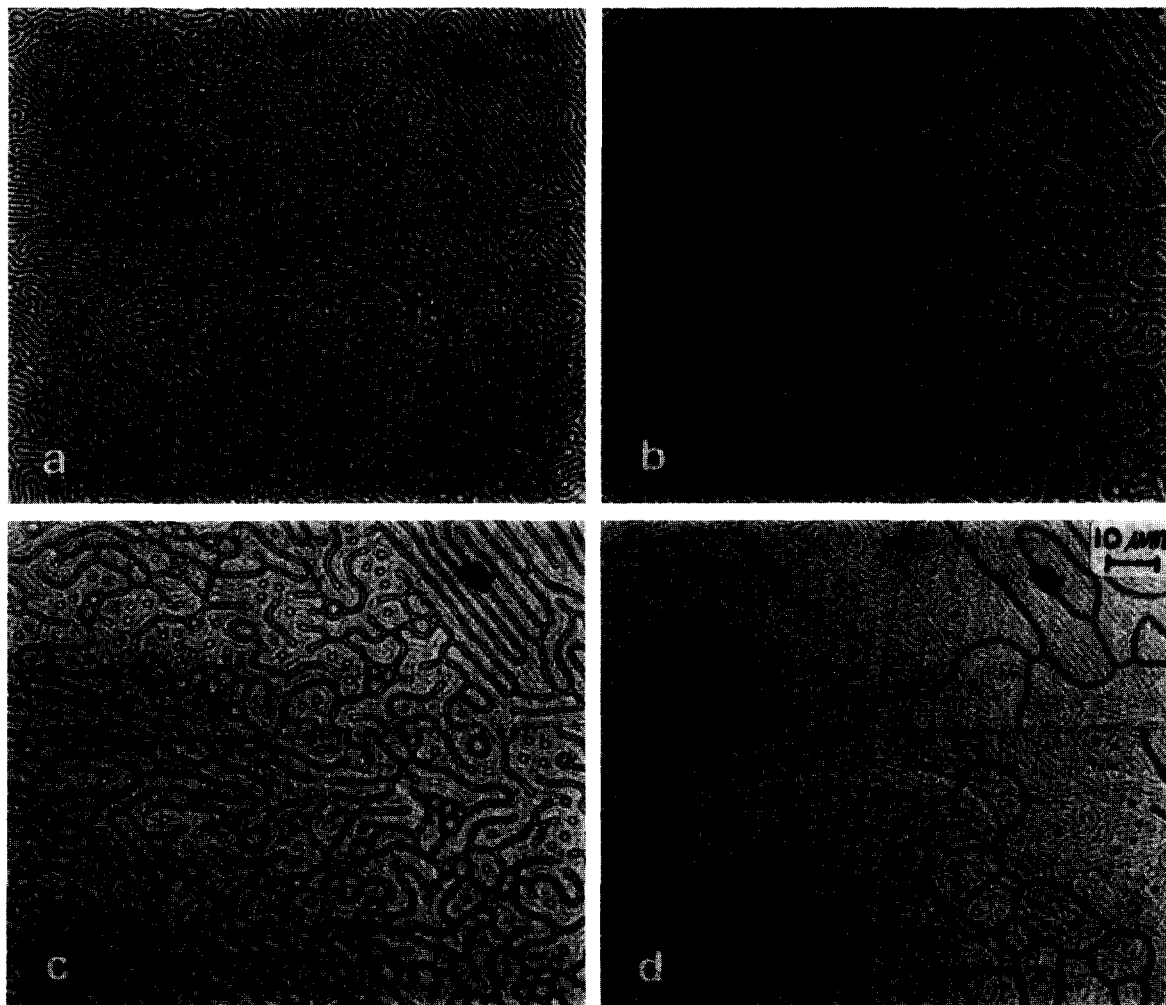


Fig. 8. Bitter domain patterns observed on a $\text{NiFe}_{2-x}\text{Al}_x\text{O}_4$ film with $x = 0.52$ grown onto $\text{Zn}(\text{Ga,Al})_2\text{O}_4$ without (a) and with an external magnetic field H perpendicular to the film; (b) $H = 95$ Oe, (c) 190 Oe, (d) 290 Oe.

the sintered material.

Since accurate thickness measurements could be performed on films grown on (111) MgO we have grown several NiFe_2O_4 films with different thicknesses. When $M_s V$ is plotted versus V , a straight line going through the origin is obtained. The slope of this line corresponds to $M_s = 235 \pm 5$ Gauss. For a NiFe_2O_4 film grown on a $\text{Zn}(\text{Ga, Fe})_2\text{O}_4$ substrate, the anisotropy as calculated from eq. (6) increases by about 50% when a 10% higher value of M_s is used.

Also the possibility of interdiffusion between film and substrate must be taken into consideration, since

substitution of Zn^{2+} and Ga^{2+} in the spinel film occurs on tetrahedral sites and will result in an increase of M_s of the film when small amounts of Zn^{2+} and Ga^{3+} are present. In a previous paper [13] we have shown that interdiffusion occurs when lithium ferrite films are grown on MgO substrates above 1000°C . Robertson et al. [14] have shown that very severe interdiffusion occurs when (Mn, Zn) Fe_2O_4 films are grown into Zn_2TiO_4 substrates, even at temperatures below 900°C , while on MgO substrates no evidence for interdiffusion was found. Interdiffusion results in broadened and/or asymme-

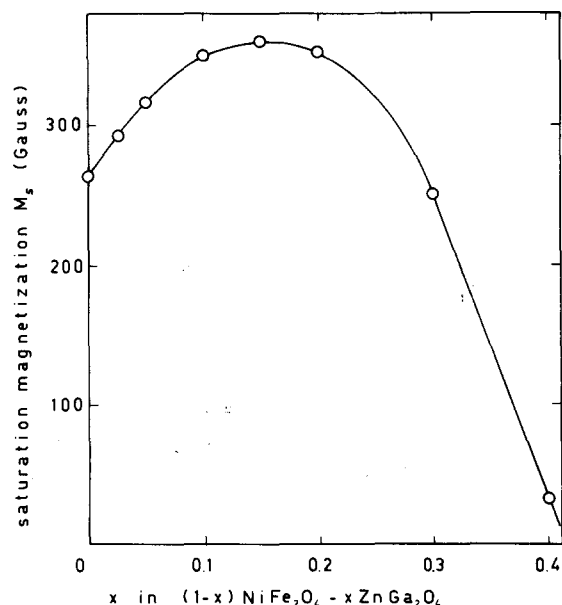


Fig. 9. Saturation magnetization M_s versus the composition in the $(1-x)\text{NiFe}_2\text{O}_4-x\text{ZnGa}_2\text{O}_4$ system.

trical X-ray reflections, which may be shifted in the direction of the substrate reflection. For our Ni(Fe, Al)₂O₄ films grown on MgO no evidence for interdiffusion, neither from X-ray nor from microprobe analyses, could be found. For films grown on spinel substrates, however, slightly asymmetrical reflections were found. Microprobe analysis performed on a 12

μm NiFe₂O₄ film grown for 30 min at 870°C onto a ZnGa₂O₄ crystal, showed that the film composition can approximately be given as $(1-x)\text{NiFe}_2\text{O}_4-x\text{ZnGa}_2\text{O}_4$. At the film-air surface x is about zero and reaches a value of about 0.03 at 2 μm from the film-substrate interface. The average film composition corresponds with $x \sim 0.01$. Using polycrystalline $(1-x)\text{NiFe}_2\text{O}_4-x\text{ZnGa}_2\text{O}_4$ samples, sintered at 1250°C in oxygen, we have determined M_s as a function of x (fig. 9). Starting with 265 Gauss for $x = 0$, M_s reaches its maximum of 360 Gauss for x is about 0.15. In view of this result, the average M_s value of the 12 μm film is about 5% higher than the value for pure NiFe₂O₄.

An improvement in the determination of the film volume was achieved by using X-ray fluorescence. The film grown on a (111) facet was dissolved in lithium borate and the amounts of Ni and Fe were determined. Since the film thickness can be assumed as a constant, when interdiffusion occurs, the volume of the film can be calculated from the density of NiFe₂O₄. The obtained accuracy is about 15% resulting in $M_s = 260 \pm 40$ Gauss for the film magnetization, which is still too inaccurate to calculate reliably the anisotropy in NiFe₂O₄ films. For NiFe₂O₄ films on MgO 235 Gauss and on spinel substrates 245 Gauss is used in the calculations of K_{μ} .

Torque measurements are performed on NiFe₂O₄ films grown on MgO and on spinel substrates with lattice constants lower and higher than NiFe₂O₄

Table 3
Anisotropy data in 10^4 erg/cm^3 for NiFe_{2-x}Al_xO₄ films; the values of M_s used in the calculations of $K_{\mu}(\text{exp})$ are expressed in Gauss

Substrate	x (film)	M_s	η	K_{μ}^s ($\eta = 0$)	K_{μ}^s ($\eta = 1$)	$K_{\mu}(\text{exp})$	$a_s - a_f$ (Å)
MgO	0	235	1	—	-18 ± 4	(-5) - (-12) ± 3	~+0.09
Zn(Ga, Al) ₂ O ₄	0	245	0.5-1	-30 ± 4	+4 ± 2	(-9) - (+6) ± 5	-0.035 ± 0.005
ZnGa ₂ O ₄	0	245	0	-4 ± 2	+3 ± 2	(-9) - (+1) ± 5	-0.002 ± 0.001
Zn(Ga, Fe) ₂ O ₄	0	245	0.2-0.5	+24 ± 5	+3 ± 2	(+26) - (+12) ± 5	+0.027 ± 0.005
ZnGa ₂ O ₄	0.10-0.12	200	0 -1	+9 ± 1	+3 ± 2	(+15) - (+3) ± 5	+0.011 ± 0.001
ZnGa ₂ O ₄	0.16-0.18	175	0 -1	+16 ± 2	+2 ± 2	(+15) - (-2) ± 4	+0.020 ± 0.002
Zn(Ga, Al) ₂ O ₄	0.16-0.18	175	0 -1	-11 ± 2	+3 ± 2	(-11) - (-3) ± 4	-0.014 ± 0.002
Zn(Ga, Al) ₂ O ₄	0.50-0.55	50	0 -0.3	+6 ± 2	+1 ± 2	(+8) - (+4) ± 3	+0.016 ± 0.005
Zn(Ga, Al) ₂ O ₄	0.55-0.60	35	0 -0.5	+7 ± 1	+1 ± 2	(+9) - (+2) ± 3	+0.023 ± 0.005
Zn(Ga, Al) ₂ O ₄	0.60-0.65	25	0.2-0.7	+7 ± 1	+1 ± 2	(+5) - (+2) ± 3	+0.030 ± 0.005

(compressively and tensively stressed films), and on Ni(Fe,Al)₂O₄ films grown in compression as well as in tension on Zn(Ga,Al)₂O₄ substrates. The results are presented in table 3 and discussed in the following section.

6. Results and discussion

The experimentally found uniaxial anisotropy data ($K_u(\text{exp})$) presented in table 3 are obtained using eq. (6). From this equation it can be seen that the accuracy of K_u decreases with increasing M_s for a fixed accuracy of KV/M_sV . In general the obtained accuracy of KV/M_sV increases with increasing M_s . The theoretical anisotropy data ($K_u^s(\eta = 0)$ and $K_u^s(\eta = 1)$) are calculated from eqs. (1) and (2) for $\eta = 0$ and $\eta = 1$. The values of η in the table are deduced from a_f and a_f^+ .

6.1. NiFe₂O₄ films

Since NiFe₂O₄ films on MgO substrates are stress relieved at the deposition temperature [3], the stress in the film results from $\Delta\alpha$ and ΔT on cooling to room temperature. K_u is found to be in the range of -5×10^4 to -12×10^4 erg/cm³ with an inaccuracy of about 3×10^4 erg/cm³, compared with $(-18 \pm 4) \times 10^4$ erg/cm³ theoretically, taking inaccuracies in $\Delta\alpha$ and ΔT into account. The difference between $K_u(\text{exp})$ and $K_u^s(\eta = 1)$ may be due to some stress relief in the film, caused by cracking. The same difference was found between experimental and theoretical anisotropy data for copper ferrite films [15] grown on MgO.

In 1973, Kanturek et al. [16] have reported about cylindrical magnetic bubbles in NiFe₂O₄ films grown onto MgO substrates by means of chemical vapour deposition. The induced anisotropy was attributed to the misfit between film and substrate. The existence of bubbles, as well as the given explanation, is in contradiction with the results reported in this article. A severe interdiffusion between film and substrate, resulting in a solid solution between MgFe₂O₄ and NiFe₂O₄ and a considerable amount of stress, perhaps results in a positive uniaxial anisotropy exceeding the demagnetization energy of the film. Interdiffusion between NiFe₂O₄ and MgO and/or the presence of

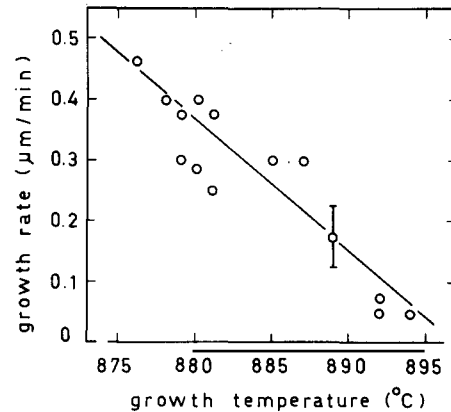


Fig. 10. Growth rate versus growth temperature for NiFe₂O₄ films grown onto Zn(Ga,Fe)₂O₄ substrates. Deposition time 5–15 min.

Fe²⁺ in the film can be concluded from the lattice parameters of “NiFe₂O₄” films grown by means of CVD [9,17,18], which are in the range of 8.38–8.42 Å compared with about 8.34 Å for pure NiFe₂O₄. When NiFe₂O₄ films on MgO are annealed at tem-

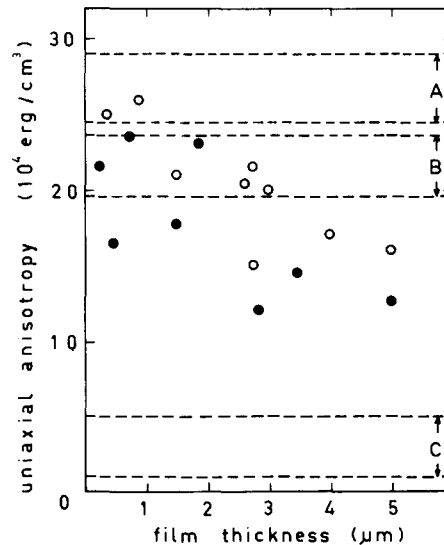


Fig. 11. Uniaxial anisotropy data versus film thickness for NiFe₂O₄ films grown onto Zn(Ga,Fe)₂O₄ substrates. (○) Misfit: 0.022–0.026 Å; (●) misfit: 0.027–0.032 Å. The theoretically calculated values of $K_u^s(\eta = 0)$ (●), $K_u^s(\eta = 0)$ (○) and $K_u^s(\eta = 1)$ are indicated by the zones A, B and C, respectively.

peratures of 1000°C and higher in oxygen, an increase of the film lattice parameter is indeed observed with increasing annealing time.

On flux-grown spinel substrates, NiFe₂O₄ films are grown between 870 and 900°C (fig. 10). Assuming a saturation magnetization M_s of 245 Gauss, the average film thickness could be determined from $M_s V$ and surface area. In fig. 11 the obtained K_u values, for NiFe₂O₄ films grown in tension on Zn(Ga, Fe)₂O₄ substrates, are plotted against the film thickness with the misfit as parameter. It can be concluded that the best agreement between $K_u(\text{exp})$ and $K_u^s(\eta = 0)$ is obtained for the thinnest films and the lowest misfits values. The fractional stress relief η was found as 0.2 for 0.5 μm films up to 0.5 for 4 μm films. When ZnGa₂O₄ substrates are used as substrates, a very small misfit is present, and up to about 6 μm film thickness, η is about zero. Although, due to the low misfit, the relative inaccuracy in $K_u(\text{exp})$ is rather large, the obtained anisotropy data are in reasonable agreement with $K_u^s(\eta = 0)$. A rather high misfit is present when NiFe₂O₄ films are grown onto Zn(Ga, Al)₂O₄ substrates resulting in a value of η between 0.5 and 1 and $K_u(\text{exp})$ between $K_u^s(\eta = 0)$ and $K_u^s(\eta = 1)$.

6.2. Ni(Fe, Al)₂O₄ films

NiFe_{2-x}Al_xO₄ films with $x = 0.10$ – 0.12 are grown in the temperature range of 890–935°C onto ZnGa₂O₄ substrates. Depending on the film thickness, η ranges from zero to 1. Positive anisotropies are obtained, covering the range between $K_u^s(\eta = 0)$ and $K_u^s(\eta = 1)$.

Films with $x = 0.16$ – 0.18 are grown between 928 and 975°C. For dipping times of 10 min, η decreases from 1 to zero with decreasing undercooling (fig. 4). The relation between growth temperature and measured uniaxial anisotropy is plotted in fig. 12, showing an excellent agreement between measured and calculated K_u values for films grown in tension as well as in compression.

Uniaxial anisotropies exceeding the demagnetization energies are obtained in films with x between 0.50 and 0.65. The very high inaccuracies in $KV/M_s V$ are compensated by the low value of M_s in the determination of K_u . The experimental K_u values are found in reasonable agreement with the calculated stress-induced anisotropy data.

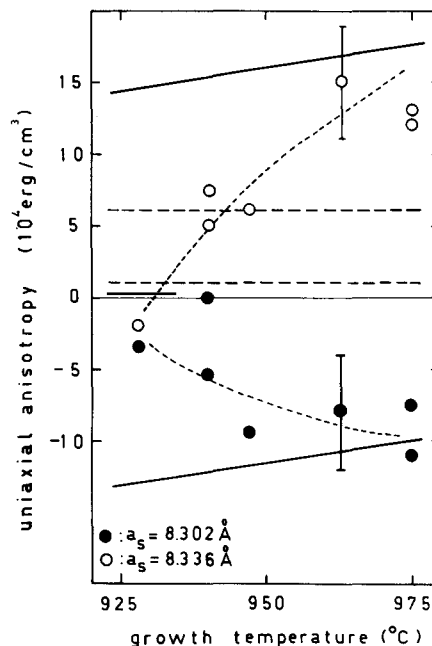


Fig. 12. Uniaxial anisotropy data for NiFe_{2-x}Al_xO₄ films with $0.16 \leq x \leq 0.18$ versus the growth temperature for films grown in tension (○) and in compression (●). Solid lines indicate theoretical K_u^s values for $\eta = 0$. The calculated values for $K_u^s(\eta = 1)$ are found in the area between the dashed lines.

7. Conclusions

Ni(Fe, Al)₂O₄ films are grown successfully by means of liquid phase epitaxy on MgO, ZnGa₂O₄, Zn(Ga, Al)₂O₄ and Zn(Ga, Fe)₂O₄ substrates from a PbO–B₂O₃ flux, using undercoolings of up to 60°C. Smooth and shiny films are obtained only on (111) substrates. At the surface of the films, grown onto the (111) facets of flux-grown substrates, many growth hillocks are present. The large defect density of the substrate will be one of the main causes for the occurrence of the hillocks.

The compositions of the films are very close to stoichiometry and the Pb content is lower than 0.02 atoms Pb per spinel formula unit. Interdiffusion between film and substrate is observed to a small extent when films are grown on the spinel substrates. It is shown that the saturation magnetization in the NiFe₂O₄–ZnGa₂O₄ system increases rapidly with increasing ZnGa₂O₄ content and a maximum is found at approximately 15 mole% ZnGa₂O₄.

Depending on the film thickness and the misfit, cracked or crack-free films are obtained. NiFe₂O₄ films grown onto MgO substrates are stress-relieved at the deposition temperature. For small film thicknesses and small lattice mismatches, elastically deformed films can be grown without stress relief on the spinel substrates.

From torque measurements it is shown that compressive films have a negative anisotropy, while positive anisotropies are found for films grown in tension. On films with positive uniaxial anisotropies, serpentine-like domain structures are observed, using Bitter fluid. Crack-free NiFe_{2-x}Al_xO₄ films with a uniaxial anisotropy energy exceeding the demagnetization energy are obtained when the misfit is lower than 0.03 Å and 0.50 < x < 0.65. In such films the serpentine-like domains can be contracted to cylindrical magnetic bubbles, with the use of an external magnetic field applied perpendicular to the plane of the film. Evidence is presented that the uniaxial anisotropy results from the misfit stress in contribution with the negative λ₁₁₁ magnetostriction constant of the film. The experimental anisotropy data are found to be in reasonable agreement with calculated values of the stress-induced uniaxial anisotropy.

Acknowledgements

The authors should like to thank Mr. H.T. Weber and Mr. K. Lodder, both of the University of Technology Twente, respectively for the X-ray fluorescence analyses and for the use of their torque magnetometer. Mr. H. de Jonge Baas and Mr. F.C. Krüger, both

of our Laboratory, are thanked for their assistance in X-ray diffractometry.

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