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LPE growth of Mn-, Ni- and Al-substituted copper ferrite films

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Single-crystalline Mn-, Ni-, and Al-substituted copper ferrite films are grown by the LPE method from a PbO-B_2O_3 flux on (111)-MgO substrates. Solid solutions between copper ferrite and Mn_3O_4, $NiFe_2O_4$, and $CuAl_2O_4$ are obtained. The segregation coefficients for Ni and Al are shown to be linearly dependent on the growth temperature. From domain-structure observations and from torque measurements it is concluded that a positive uniaxial anisotropy is present in the copper ferrite films. After stress relief at the deposition temperature a stress develops during cooling to room temperature due to a difference in thermal expansion coefficients of film and substrate. This stress is responsible for the observed anisotropy.

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I. INTRODUCTION

In a previous article concerning the liquid-phase epitaxial growth of copper ferrite films[1] we attempted to give an explanation for the serpentinelike domain pattern observed after applying Bitter fluid to the surface of copper ferrite films grown on (111)-MgO substrates. From annealing experiments, a growth-induced anisotropy could almost be excluded and the misfit-induced uniaxial anisotropy (assuming only elastic deformation of the film!) was calculated to be negative (film under tensile stress together with a positive magnetostriction constant for copper ferrite). We believed that a possible explanation of the domain structure of the film could be found in a tetragonal distortion of the epitaxial layer, although from x-ray analysis no evidence for this distortion could be found.

In this article we present our results obtained with Mn-, Ni-, and Al-substituted copper ferrite films. These results will shed some light into the origin of this anisotropy.

II. THE GROWTH OF MANGANESE-SUBSTITUTED COPPER FERRITE FILMS

A better fit between the lattice constants of $MgO(2a_0 = 8.42\ \text{Å})$ and copper ferrite ($a_0 = 8.38\ \text{Å}$) can be obtained when Cu or Fe are substituted by Mn. At the same time the saturation magnetization is lowered. The addition of Mn_3O_4 to copper ferrite promotes the formation and/or stabilization of the cubic structure.[2] According to Delorme[3] solid solutions containing 1.5–55 mole % Mn_3O_4 are always cubic.

The films were grown from a supersaturated melt, composed of 1 PbO, 0.25 B_2O_3, 0.08 CuO +0.15 $CuFe_2O_4$ + x Mn_2O_3 (moles), by vertically dipping for 10 min on syton-polished (111)-MgO substrates. Addition of Mn_2O_3 to the melts results in an increase in the saturation temperature. Films with a thickness in the range 2–9 μm were obtained using growth temperatures between 820 ($x = 0$) and 940 °C ($x = 0.42$).

Lattice constants, saturation magnetization, and compositions of the films were determined and reported previously.[4] In Fig. 1 we have plotted the compositions of the films versus the amount of Mn_2O_3 in the melt. With increasing Mn_2O_3 content in the melt, higher growth temperatures are used and, as a consequence, the Pb content in the films decreases. Although the manganese is added as Mn^{3+} to the melt, the composition of the film is a solid solution between $Mn^{2+}Mn_2^{3+}O_4$ and copper ferrite: From Fig. 1 it follows that for each three Mn ions two Fe ions and one Cu ion are replaced. The lattice constants and the saturation magnetization are plotted in Fig. 2 as a function of the amount Mn ions per spinel formula unit. The serpentinelike domain pattern, which can be observed after applying Bitter fluid to the surface of copper ferrite films, can also be observed for films composed of a solid solution between Mn_3O_4 and copper ferrite. Although the pattern becomes more diffuse with increasing manganese content, it is still present for those com-

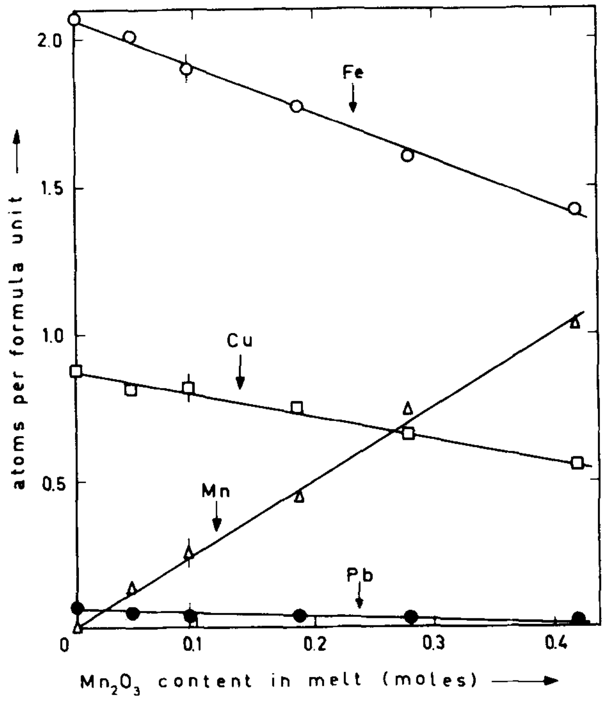

FIG. 1 Compositions of Mn-substituted copper ferrite films versus the amount of Mn_2O_3 in the melt per mole PbO.

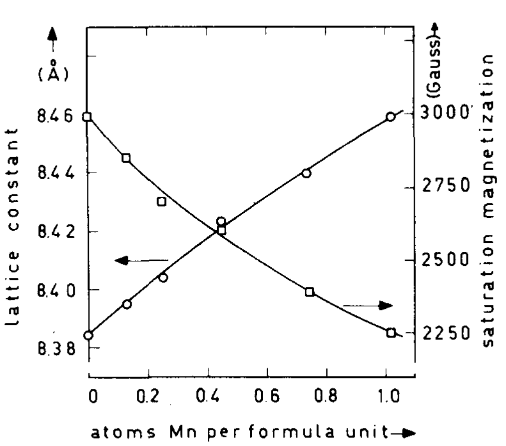

FIG. 2. Lattice constants and saturation magnetizations for Mn_3O_4-copper ferrite films versus the amount of Mn per spinel formula unit.

positions, which are always cubic according to Delorme.[3] In view of this result a tetragonal distortion being the origin of the domain pattern is difficult to believe.

III. STRESS RELIEF OF EPITAXIAL FILMS

According to the stress model, developed by Besser *et al.*,[5] two mechanisms are possible for the accomodation of the misfit between the substrate and the film. For small misfit values the film is strained elastically to bring the lattices of film and substrate into register at the interface. For higher misfit values at the deposition temperature 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 at the deposition temperature by the formation of misfit dislocations.[6] When the films are considered to behave elastically on cooling to room temperature, a stress σ develops as a result of the differences in thermal expansion coefficients between film (α_f) and substrate (α_s). The resulting room temperature stress σ in the film can be given as

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

where a_s and a_f are the bulk room-temperature lattice parameters of substrates and films, respectively, ΔT is the difference between deposition temperature and room temperature, E is Young's modulus, ν is the Poisson ratio, and η is the fractional stress relief ($0 < \eta < 1$). The stress-induced anisotropy energy can be calculated as

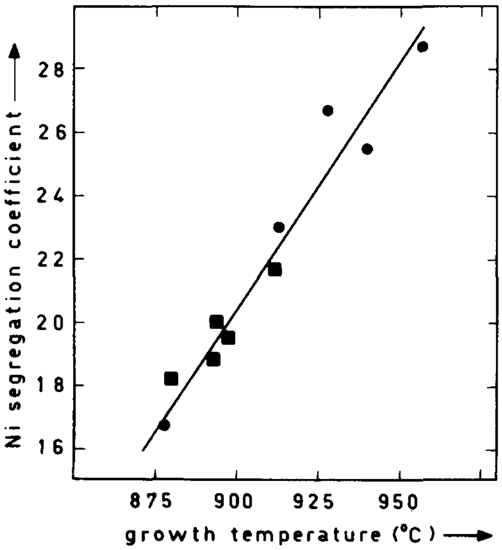

FIG. 3. The segregation of coefficient for Ni versus the growth temperature ($NiFe_2O_4$-copper ferrite films).NiO concentrations in the melt: 0.003 (■) and 0.006 moles NiO (●) per mole PbO.

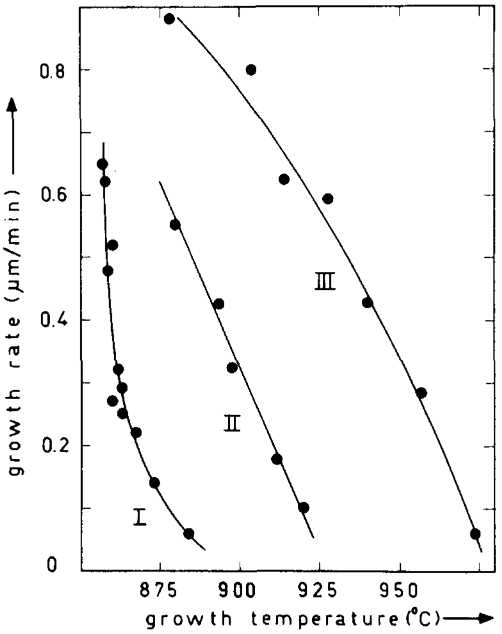

FIG. 4. Growth rate versus the growth temperature for $NiFe_2O_4$-copper ferrite films grown during 10 min. I: copper ferrite; II and III: $NiFe_2O_4$-copper ferrite after addition of respectively 0.003 and 0.006 moles NiO to the melt.

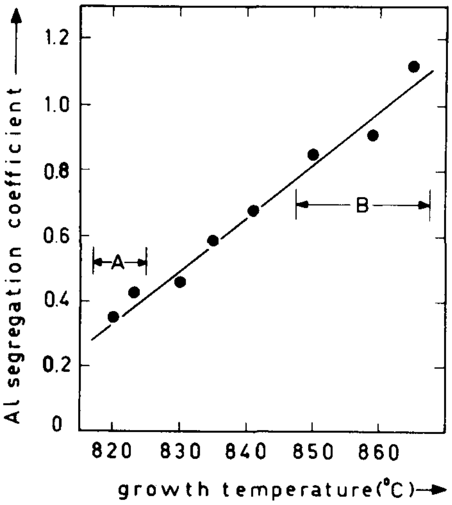

FIG. 5. The segregation coefficient for Al versus the growth temperature-(copper ferrite-aluminate films). Al_2O_3 concentrations in the melt per mole PbO: With increasing growth temperature. 0.017 (points A), 0.034, 0.068, 0.085, and 0.105 (points B) moles Al_2O_3.

$$K_u = -\tfrac{3}{2}\lambda_{111}\sigma. \tag{2}$$

Since the strain energy increases with increasing film thickness, there is a critical thickness h_c above which it becomes energetically favorable to form misfit dislocations. Matthews and Klokholm[7] have calculated h_c for garnet thin films as a function of the fractional misfit.

$$f = (a_s - a_f)/a_f, \tag{3}$$

$$h_c = (b/8\pi|f|)(1+\nu)[\ln(r/b)+1], \tag{4}$$

where b is the Burgers vector, ν is the Poisson ratio, and r is the dislocation strain field radius.

We have applied Eqs. (3) and (4) to our spinel ferrite films.

At a growth temperature of about 800 °C there is a large difference between the lattice constants of copper ferrite ($a \sim 8.45$ Å) and MgO ($2a \sim 8.52$ Å), resulting in a fractional misfit of 8.3×10^{-3}. When b is assumed to be equal to the lattice constant of the film at the deposition temperature, ν is taken as 0.3, and r is taken between 0.1 and 10 μm, a critical thickness between 2.5×10^{-2} and 4.5×10^{-2} μm results. Since our copper ferrite films have thicknesses ranging from 1 to 10 μm, stress relief will occur at the deposition temperature ($\eta = 1$).

Apart from the formation of misfit dislocations, at sufficiently high misfit values, the formation of cracks can contribute to the stress relief. This may occur at the deposition temperature as well as during the cooling to room temperature, resulting in a lower value of σ than calculated from $\Delta\alpha$. Commonly, 100% elastically deformed films ($\eta = 0$) are in compression when $a_f > a_s$ and in tension when $a_f < a_s$. However, when 100% stress relief occurs at the deposition temperature ($\eta = 1$) only the differences in thermal expansion coefficients of substrate and film dictates whether the films are in compression ($\alpha_f < \alpha_s$) or in tension ($\alpha_f > \alpha_s$) at room temperature. This means that compressive films can be obtained for $\eta = 1$ even when $a_f < a_s$.

In a previous work concerning the LPE growth of $NiFe_{2-x}Al_xO_4$ films[4] we have shown that films grown on (111)-MgO substrates ($a_f < a_s$) are stress relieved at the deposition temperature. Due to the compressive nature of the films ($\alpha_f < \alpha_s$), the room-temperature lattice parameters of the films, as determined from the Bragg angles of planes parallel to the film surface, are higher than the room-temperature lattice parameters of stress-free corresponding compositions. The Pb content in the films was shown to be lower than 0.02 atoms Pb per spinel formula unit. The difference in film lattice parameter, however, is smaller than expected from $\Delta\alpha$ and ΔT when stress relief occurs at the deposition temperature followed by 100% elastic deformation of the film on cooling to room temperature. Obviously, some stress is relieved by the formation of cracks. Some cracking has indeed been observed at the film surface.

In our LPE study concerning the growth of lithium ferrite-aluminate[8] stress relief also has to be expected when films are grown on MgO. We have found no deviations between the lattice constants of films and corresponding spinel compositions although larger film values are expected. Severe film cracking was also not observed. Glass and Liaw[9] have found cracks in LPE-growth lithium ferrite films grown on spinel substrates even when low misfit values were used. They found indications that these cracks were formed during the cooling of the film and substrate to room temperature.

IV. THE GROWTH OF NICKEL-SUBSTITUTED COPPER FERRITE FILMS

The serpentinelike domain pattern observed on the surface of copper ferrite films grown by means of LPE on MgO substrates and the small positive value of K_u found from torque measurements[1] can be explained assuming stress relief at the deposition temperature followed by elastic deformation of the layer on cooling to room temperature since $\alpha_f < \alpha_s$ and $\lambda_{111} \simeq +10^{-5}$ for copper ferrite.[10] Because λ_{111} for nickel ferrite[11] is -2.1×10^{-5}, substitution of Cu^{2+} by Ni^{2+} in copper ferrite films should have a pronounced effect on the stress-induced anisotropy as well as on the domain pattern.

The film growth was performed on (111)-MgO substrates by vertically dipping for 10 min in a supersaturated melt composed of 1 PbO, 0.25 B_2O_3, 0.08 CuO +0.20 $CuFe_2O_4$ (moles) to which small amounts of NiO were added (0.003 and 0.006 moles). These small additions of NiO had a very pronounced effect on the saturation temperature of the melt; e.g., the addition of 0.006 moles NiO gave an increase of about 100 °C. With these melts very large supersaturations, up to about 100 °C, could be used. The growth temperature has a strong influence on the amount of Cu which is substituted by Ni; e.g., with NiO = 0.006 moles at 878 °C $Cu_{0.63}Ni_{0.34}Pb_{0.02}Fe_{2.01}O_4$ is obtained, while at

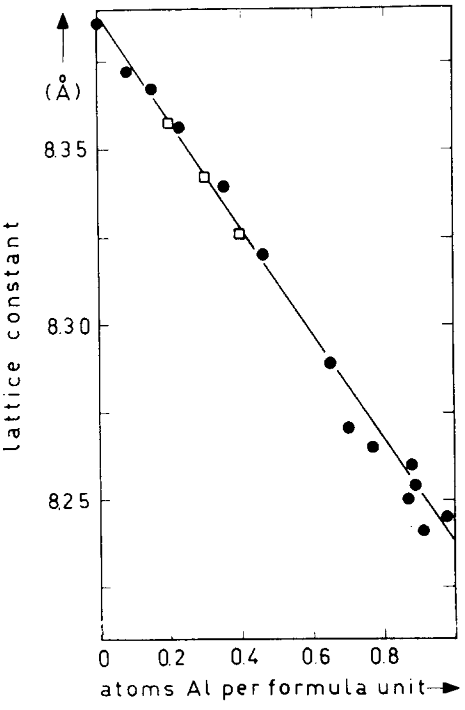

FIG. 6. The lattice constants of copper ferrite-aluminate films versus the Al-content (●) together with the values obtained for sintered $Cu_{0.95}Fe_{2.05-x}Al_xO_4$ standards (□).

957 °C $Cu_{0.39}Ni_{0.59}Pb_{0.01}Fe_{2.01}O_4$ is obtained. The segregation coefficient for Ni, defined as the mole ratio

$$k_{Ni} = \frac{[Ni/Ni + Cu)]_{film}}{[Ni/(Ni + Cu)]_{melt}}, \tag{5}$$

is plotted in Fig. 3 versus the growth temperature. The same temperature dependence is found for both Ni concentrations in the melt. It has to be noted that the segregation coefficients are calculated for films grown with different growth rates. The relation between growth rate and growth temperature is plotted in Fig. 4.

The very high value for k_{Ni} can be attributed to the high CuO concentration in the melt, which is necessary to prevent nucleation of $PbFe_{12}O_{19}$. For the growth of pure $CuFe_2O_4$ for instance a $CuO:Fe_2O_3$ mole ratio of 1.4 is used, while for the growth of $NiFe_2O_4$ a $NiO:Fe_2O_3$ mole ratio of about 0.1 can be used.[4]

When the Ni content in the film is increased above about 0.25 atoms Ni per formula unit, the serpentinelike domain pattern, as observed on copper ferrite layers, is no longer observed. If a linear relationship is assumed between composition and λ_{111} in the $Cu_{1-x}Ni_xFe_2O_4$ system, λ_{111} will be zero for $x \sim 0.33$. Since the thermal expansion coefficients for both $CuFe_2O_4$ and $NiFe_2O_4$ are smaller than for MgO, a positive anisotropy will be present for $x \lesssim 0.33$ and a negative anisotropy for $x \gtrsim 0.33$. From torque measurements we find a small positive anisotropy for $x = 0$ and a small negative anisotropy for $x = 1$ [$NiFe_2O_4$ grown on MgO (Ref. 4)].

From these results, evidence is found for the concept of stress relief at the deposition temperature followed by stress formation during the cooling to room temperature.

V. THE GROWTH OF COPPER FERRITE-ALUMINATE FILMS

Bulk $Cu_{0.95}Fe_{2.05-x}Al_xO_4$ cannot be obtained in the tetragonal phase by slow cooling for $x > 0.3$. By substitution of Fe by Al the lattice constant as well as the saturation magnetization are lowered.

The film growth was accomplished from 1 PbO, 0.25 B_2O_3, 0.11 CuO +0.15 $CuFe_2O_4$ melt (moles) to which up to 0.105 moles Al_2O_3 were added. For higher Al contents, $Pb(Fe,Al)_{12}O_{19}$ was obtained as a second phase. The addition of Al_2O_3 to the melt raises the saturation temperature.

At 805 °C, without Al_3O_3 addition to the melt, a composition $Cu_{0.87}Fe_{2.07}Pb_{0.06}O_4$ was found from microprobe analysis, while at 865 °C, after addition of 0.105 moles Al_2O_3, a film composition of $Cu_{0.95}Fe_{1.07}Al_{0.96}Pb_{0.02}O_4$ was obtained: The Pb content decreases with increasing temperature, while the Cu content goes toward unity with increasing Al content. The segregation coefficient for Al, defined as the mole ratio

$$k_{Al} = [Al/(Al + Fe)]_{film} / [Al/(Al + Fe)]_{melt}, \tag{6}$$

is plotted versus the growth temperature in Fig. 5. An approximately linear relation is obtained. The growth rates of the films were in the range 0.3–0.7 μm/min. The segregation coefficients were calculated for films grown from melts with different Al concentrations in the melt. The lattice constants and the saturation magnetization are plotted versus the Al content in Figs. 6 and 7. Since $\alpha(CuFe_2O_4) < \alpha(MgO)$, the lattice constants of the films, as mesaured on the MgO substrates, should be larger than the constants for corresponding compositions assuming elastic deformation of the films when cooling to room temperature. The lattice constant of our copper ferrite film (8.386 Å), as measured on the substrate, is higher than the value reported for cubic $CuFe_2O_4$ (8.369 Å).[12] This higher lattice constant, however, can also be attributed to the influence of lead and ferrous ions in the film. The lattice constants of the sintered standards of cubic $Cu_{0.95}Fe_{2.05-x}Al_xO_4$, quenched from 1100 °C, are very close to the film lattice constants. In view of the variations in composition it is very hard to conclude whether or not our film lattice constants are higher than their corresponding stress-free compositions. Since there are very few cracks in the film, we believe that at least a large part of the stress induced by the differences in thermal expansion coefficients must be present in the film.

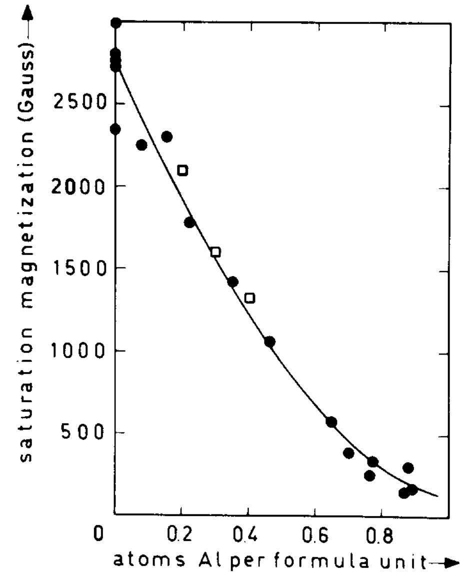

FIG. 7. The saturation magnetization ($4\pi M_s$) of copper ferrite aluminate film versus the Al content (●). Open symbols (□) represent sintered standards.

We have performed torque measurements on (111)-copper ferrite-aluminate films. After correction for demagnetization ($2\pi M_s^2$), positive values for the uniaxial anisotropy remained. When this uniaxial anisotropy K_u is plotted versus the Al content a linear relation is obtained (Fig. 8). For Al contents larger than 0.6 atoms Al per formula unit the uniaxial anisotropy energy exceeds the demagnetization energy ($2\pi M_s^2$). When the films with $K_u > 2\pi M_s^2$ are brought into a magnetic field, the film plane orientates itself perpendicular to the direction of the magnetic field. This clearly shows that the film normal is the easy axis of magnetization. In view of the very large misfit in this system only the stress generated during the cooling from the deposition temperature can be the cause of this uniaxial anisotropy.

The domain pattern as observed on the surface of copper ferrite films becomes weaker when the Al content of the

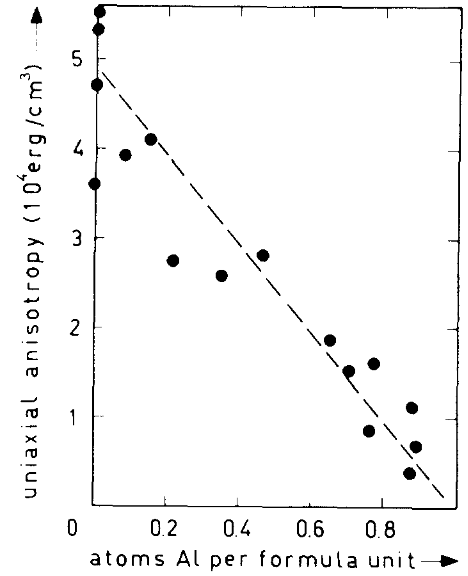

FIG. 8. The uniaxial anisotropy versus the Al-content for copper ferrite - aluminate film grown on (111) – MgO substrates.

film is increased and disappears completely when the Al content is increased above 0.9 atoms Al per formula unit.

This behavior is consistent with the decrease of K_u with increasing Al content in the film and with the decrease of $4\pi M_s$, which approaches zero for $x = 0.9$. The decrease of K_u will mainly be due to a decrease of λ_{111}. This means that λ_{111} for copper ferrite-aluminate decreases approximately linear with increasing Al content and becomes zero for ~ 0.9 atoms Al per spinel formula unit.

According to Arai and Tsuja[10] the magnetostriction constant of copper ferrite is dependent on the quenching temperature (T_q). Using a capacitance method they obtained values ranging from 8.8×10^{-6} ($T_q = 950$ °C) up to 1.38×10^{-5} ($T_q = 820$ °C). Petrakovskii *et al.*[13] obtained a value of 4.7×10^{-6} ($T_q = 800$ °C) using ferromagnetic resonance.

We have determined the thermal expansion coefficients for MgO and $CuFe_2O_4$ using high-temperature x-ray diffractometry. Values of $(1.3 \pm 0.05) \times 10^{-5}$ and $(1.0 \pm 0.1) \times 10^{-5}$ K^{-1} are obtained for respectively MgO (Ref. 14) and $CuFe_2O_4$.

When λ_{111} is taken as 10^{-5} and ΔT as 800 °C, the anisotropy, assuming stress relief at the deposition temperature, is calculated for copper ferrite films grown on (111)-MgO substrates as $+8 \times 10^4$ erg/cm^3. From the torque measurements a value for copper ferrite is estimated of about $+5 \times 10^4$ erg/cm^3. In view of the uncertainties regarding the λ_{111} value for copper ferrite and the uncertainty in the amount of stress which is relieved by the formation of cracks in the film, there is a reasonable agreement between measured and calculated values.

VI. CONCLUSIONS

Mn-, Ni, and Al-substituted copper ferrite films are grown successfully by means of liquid-phase epitaxy on (111)-MgO.

We have shown that when Mn_2O_3 is added to a PbO-B_2O_3-CuO-Fe_2O_3 melt LPE films composed of a solid solution between Mn_3O_4 and copper ferrite are obtained. The serpentinelike domain patterns observed on the surface of (111)-manganese-substituted copper ferrite films cannot be explained by a positive uniaxial anisotropy, caused by a small tetragonal deformation of the layer, since the pattern can still be observed on films, which are reported to be cubic. Also a growth-induced anisotropy can be excluded from annealing experiments. We have shown that the anisotropy in all our films results from stress relief at the deposition temperature followed by stress formation due to differences in thermal expansion coefficients between film and substrate and the temperature difference between deposition temperature and room temperature. A positive uniaxial anisotropy is found when films, with a positive magnetostriction constant, are in compression at room temperature. When stress relief occurs at the deposition temperature ($\eta = 1$) compressive films are obtained at room temperature only if $\alpha_s > \alpha_f$, despite of the fact that the lattice parameter of the substrate is larger than the lattice parameter of the film, which would put the films in tension when elastic deformation occurs at the deposition temperature ($\eta = 0$).

Domain-structure observations and results obtained from torque measurements for Ni-substituted and Al-substituted copper ferrite films are consistent with the presented mechanism ($\eta = 1$).

In most cases the uniaxial anisotropy energy (K_u) is smaller than the demagnetization energy ($2\pi M_s^2$), but in copper ferrite-aluminate films with an Al content exceeding 0.6 atoms Al per spinel formula unit $K_u > 2\pi M_s^2$, resulting in an easy axis of magnetization perpendicular to the plane of the film.

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