Liquid phase epitaxial growth of indium substituted magnesium ferrite films

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LIQUID PHASE EPITAXIAL GROWTH OF INDIUM SUBSTITUTED MAGNESIUM
FERRITE FILMS

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ABSTRACT

Single crystal films of $\text{Mg}(\text{Fe},\text{In})_2\text{O}_4$ have been grown by means of liquid-phase-epitaxy on (100)- MgO substrates using a $\text{PbO}-\text{B}_2\text{O}_3-\text{Fe}_2\text{O}_3$ solvent. The final polishing of the substrates appeared to be very important in connection with the necessary large supersaturation of the flux. Electron microprobe analysis revealed Pt and high Pb contents in our films. The easy axis of magnetization is in-plane, probably due to the compressive strain of the films caused by the difference in thermal expansion of MgO and $\text{Mg}(\text{Fe},\text{In})_2\text{O}_4$.

Introduction

Magnetic films have attracted much interest because of their potential applicability in magnetic and magneto-optic devices. Most studies concern the liquid-phase-epitaxial (LPE) growth of garnet films (1) and recently the LPE growth of hexagonal ferrites has been reported (2,3). Concerning the growth of spinel ferrites most work, so far, has been done by means of chemical vapor deposition (CVD). In view of the very limited amount of LPE spinel studies (4,5) we have started a program to investigate the growth of spinel ferrite films. In this work we want to report on the growth conditions of indium substituted magnesium ferrite by means of LPE.

A basic requirement for hetero-epitaxial growth is a close match of lattice spacing between overgrowth and substrate. For the growth of spinel ferrites non-magnetic compounds with spinel structure e.g. MeGa_2O_4 ($\text{Me}=\text{Ni},\text{Mg},\text{Zn},\text{Cu}$) would be suitable as substrates. However, until now, apart from MgAl_2O_4 ,

no single crystals of adequate size have been available. For most ferrites the use of MgAl_2O_4 ($a_0 = 8.09 \text{ \AA}$) as a substrate is not attractive since the lattice mismatch is too large. Instead, we have used MgO which is commercially available. Magnesia has a lattice constant of $4.21 \text{ \AA}$, and eight unit cells fit perfectly to a spinel cell with $a = 8.42 \text{ \AA}$. If one is interested in films which can sustain magnetic bubbles there are additional requirements both to the substrate and the overgrowth itself. For this purpose the film must have a uniaxial anisotropy K_u with the preferred axis perpendicular to the plane of the film. The uniaxial anisotropy field $H_k = K_u/2M_s$ has to be larger than the demagnetization field $4\pi M_s$. A low value of the saturation magnetization M_s is helpful in this respect. The anisotropy can be either growth-induced or stress-induced.

We have focussed our attention to MgFe_2O_4 as overgrowth and MgO as substrate. The lattice constant of MgFe_2O_4 (high temperature form) is $a = 8.39 \text{ \AA}$, close to the value of $8.42 \text{ \AA}$ for eight unit cells of MgO . A better fit of lattice constants between film and substrate can be accomplished by substitution of In, Sn or Ti in the film. A disadvantage of MgO as substrate is its rather high thermal expansion coefficient (6) compared with spinel ferrites. Also in this regard MgFe_2O_4 approaches MgO the best (7). Compared to other spinel ferrites the saturation moment of MgFe_2O_4 is relatively low ($4\pi M_s \sim 1500 \text{ G}$), and growth-induced uniaxial anisotropy of flux-grown bulk crystals of Al-substituted MgFe_2O_4 has been reported (8).

Experimental

The thermal expansion of MgO and In, Sn or Ti substituted MgFe_2O_4 has been determined using high temperature diffractometry. Substitution is accomplished in such a way that the room temperature lattice constants are about twice the value of MgO . From the results, summarized in Table I, it can be concluded that the best thermal expansion fit with MgO is obtained for In-substituted MgFe_2O_4 . The accuracy of the determined lattice constants is $\pm 0.002 \text{ \AA}$.

TABLE I

Temperature dependence of lattice parameters ($\text{\AA}$) expressed as $a = a_0 + bT + cT^2$ (T in $^\circ\text{C}$) of MgO and In, Sn or Ti-substituted MgFe_2O_4 ($20 - 1200^\circ\text{C}$).

compound	a_0	$b \times 10^5$	$c \times 10^8$
MgO	4.212	5.44	0.41
$\text{MgFe}_{1.81}\text{In}_{0.19}\text{O}_4$	8.425	7.53	1.77
$\text{Mg}_{1.18}\text{Fe}_{1.64}\text{Sn}_{0.18}\text{O}_4$	8.428	7.86	0.83
$\text{Mg}_{1.50}\text{Fe}_{1.00}\text{Ti}_{0.50}\text{O}_4$	8.424	3.98	4.18

We have used a $\text{PbO-B}_2\text{O}_3\text{-Fe}_2\text{O}_3$ flux for the LPE growth of magnesium ferrite. Fig. 1 gives a survey of literature data on solvent compositions used for LPE growth of garnet films and for flux growth of bulk MgFe_2O_4 crystals (8, 9-15). In the figure the relevant part of the pseudo-ternary phase diagram is shown. The composition of the solvent used in our LPE study of MgFe_2O_4 films, as indicated by point H in Fig. 1, is 1 PbO : 0.081 B_2O_3 : 0.035 Fe_2O_3 (moles). To this solvent 0.066 moles of pre-reacted $\text{MgFe}_{1.78}\text{O}_{4.22}$ powder was added per one mole of PbO . The flux constituents were mixed and premelted in a 75 ml Pt crucible. Actually 1% PbO was replaced by PbO_2 for protection of the platinum (16). Isothermal dipping of the substrates is performed according to standard LPE garnet procedures in a vertical 3-zone resistance furnace.

MgO single crystals were obtained from Spicer Ltd., England. The crystals were X-ray oriented within 0.5° and cut into (100)-wafers, with a diameter of 12 mm and a thickness of 0.8 mm. The slices were polished with diamond pastes with successively decreasing particle sizes ranging from 30 to $0.25\ \mu\text{m}$. As will be shown later, a final treatment with Syton-W-30 was necessary. Prior to the film growth the substrates were cleaned with organic solvents. After growth termination, the adhering flux droplets are dissolved in a mixture of hot dilute acetic acid with nitric acid. Measurements of the lattice constant mismatch are made by scanning the (800)-spinel reflection and the (400)- MgO reflection with $\text{Fe-K}\alpha$ radiation.

The misfit is obtained from the relation

$$\Delta a/a = \frac{1 - \nu}{1 + \nu} \cdot \frac{\Delta\theta}{\tan \theta}. \text{ Here } \Delta a = a_s - a_f, \text{ is the difference}$$

between the unstrained lattice parameters of substrate and film, θ is the Bragg reflection angle and ν is the Poisson ratio, which is assumed to be 0.25 (17). Film thickness is measured by grinding a spherical hole, just through the film, using a 40 mm steel ball coated with diamond polishing compound and measuring the diameter of the concentric circles formed by the film surfaces. Results were checked by interferometric measurements.

FIG. 1

Part of the ternary phase diagram $\text{PbO-Fe}_2\text{O}_3\text{-B}_2\text{O}_3$. Solvent compositions in mol % used for flux growth and solubility studies of MgFe_2O_4 and for LPE garnet studies. A ref. 10; B ref. 11; C ref. 8; D ref. 12; E ref. 13; F ref. 9; G ref. 14; H ref. 15, this work

Results

After stirring the melt for about 100 h at 1000°C all solid particles were dissolved, but after cooling to about 900°C tiny crystals could be observed floating on top of the melt. These crystals had an octahedral shape and could be identified as slightly In, Pb and Pt substituted MgFe_2O_4 ($a_o = 8.425 \pm 0.005 \text{ \AA}$). Electronmicroprobe analysis indicated MgO inclusions in some of these crystals. Continuous stirring of the melt at elevated temperatures diminished the amount of solid particles at lower temperatures but the particles never disappeared completely. Obviously some spontaneous nucleation occurs during cooling below the liquidus temperature of the melt.

From our first LPE experiments two features became clear. Firstly a rather large supersaturation of the flux is necessary to nucleate film growth, and secondly the surface finish of the MgO substrates is extremely important. We consider the latter point in more detail. At temperatures between 900°C and 850°C a badly adherent overgrowth was obtained on the diamond polished substrates, while on the syton polished substrates no growth could be observed. At lower temperatures we achieved a firmly adherent film on the diamond polished substrates. This overgrowth, however, looked very rough and opaque. Film growth on the syton polished substrates started only at temperatures below approximately 780°C. Often island growth was observed (Fig. 2) with crystallites in the form of identically oriented truncated pyramids with basal edges along $\langle 100 \rangle$ directions. At temperatures between 675°C and 750°C a closed, smooth and transparent, red colored overgrowth was obtained. Solidified adherent flux droplets locally spoiled the otherwise completely shiny surfaces. As shown in Fig. 3 the growth rates showed a quite different temperature dependence for the syton and diamond polished substrates. On the diamond polished substrates

FIG. 2

Island growth on a syton polished MgO substrate, growth temperature 808°C.

FIG. 3

Growth rates as a function of growth temperature for a diamond polished substrate (dashed line) and for a syton polished substrate (solid line).

FIG. 4A

FIG. 4B

Stereoscan picture of a film grown on a diamond polished substrate (a) or on a syton polished substrate (b).

the growth rate decreased linearly from $0.9 \mu\text{m}/\text{min}$ at 850°C to less than $0.1 \mu\text{m}/\text{min}$ at 700°C . For the syton polished substrates the growth rate showed a maximum of about $0.5 \mu\text{m}/\text{min}$ near 760°C (dipping time 5 min.). The difference in growth behavior must be due to the surface morphology of the substrates. Stereoscan pictures reveal a much smoother MgO surface for the syton polished substrates compared with the diamond polished substrates. This difference in surface morphology is clearly reflected in the respective film surfaces. Fig. 4a shows the surface of a rough, opaque film grown on a diamond polished substrate. The picture shows a rather open structure, looking like a crocket-work, with needles pointing along $\langle 100 \rangle$ directions. Fig. 4b shows the surface of a transparent film grown on a syton polished substrate. The structure is more dense and rather flat in this case. The surface morphology of areas with after-growth on an otherwise smooth surface is identical with that shown in Fig. 4a.

Fig. 5 shows the growth rate of films grown on syton polished MgO , by means of horizontal dipping at a rotation speed of 125 rpm, or by vertical dipping. Rotation of the substrate during the growth produces a much smoother overgrowth and less contamination of the surface by flux drop-

FIG. 5

Growth rate as a function of growth temperature of films grown on syton polished MgO . Circles, vertically dipped; triangles, horizontally dipped with substrate rotation 125 rpm.

lets. The flatness of the horizontally dipped film was 1-2 fringes in Na-D light, compared with 5-10 fringes for the films grown by vertical dipping. There also is a different temperature dependence on the growth rates for the two cases shown in the figure.

X-ray analysis

X-ray diffraction patterns of the films were investigated by means of a Siemens texture goniometer. Pole figures of one or more forms of lattice planes can be obtained of both substrate and film by a proper selection of the Bragg angle θ . The $\{111\}$ -poles of MgO cannot be distinguished from the $\{222\}$ -spinel poles, but the $\{220\}$ -poles of the spinel appear alone. From the resulting pole figure we conclude that the films are single crystalline. For the films grown on syton polished substrates the $\langle 100 \rangle$ directions of film and substrate coincide. However, the opaque films grown on diamond polished MgO show a difference $1-2^\circ$ between the $\langle 100 \rangle$ directions of film and substrate. Due to this difference the misfit cannot be measured because MgO and spinel reflection cannot be achieved for the same platelet setting in the diffraction equipment.

The unstrained misfit $\Delta a = a_s - a_f$, between substrate and film, is plotted in Fig. 6 as a function of growth temperature T_g for films grown on syton polished MgO. All films are in compression i.e. $\Delta a < 0$. For films grown without rotation the misfit increases from $\Delta a = -0.019$ for $T_g = 800^\circ$ to $\Delta a = -0.036$ Å for $T_g = 730^\circ\text{C}$. For films grown under rotation the misfit is always 0.01 larger. Due to the difference in thermal expansion coefficient of substrate and film, a zero misfit at the growth temperature leads to a film under compression at room temperature. For $T_g = 800^\circ\text{C}$ the resulting room temperature misfit is $\Delta a = -0.0170$ Å, while for $T_g = 700^\circ\text{C}$ $\Delta a = -0.0165$ Å. From Fig. 6 it follows that the films are close to zero misfit or slightly in compression at T_g . The higher compressive strain of the films grown under rotation is probably related to the higher growth rate.

FIG. 6

Misfit, a (substrate) - a (film), as a function of growth temperature. Circles, vertically dipped; triangles, horizontally dipped with substrate rotation 125 rpm; dipping time 15 min.

Microprobe analysis

Generally differences in lattice constants are caused by differences in composition. From studies on LPE grown garnet films it is known that appreciable amounts of Pb can be incorporated (18). Indeed, x-ray fluorescence measurements revealed the presence of a large amount of Pb in our spinel films. In order to obtain more quantitative information about the chemical

composition we have performed an electron microprobe analysis. The measurements were performed using a SEM II A electronprobe micro-analyser. The concentrations were calculated with the aid of a computer program using measured intensities of pure Fe, In, Pb, Pt and MgO as standards. To optimize the experimental conditions and to check the accuracy of the results standards of sintered $\text{MgFe}_{2-x}\text{In}_x\text{O}_4$ ($x=0, 0.1, 0.2, 0.3$) were measured. For the determination of Mg a low accelerating voltage is preferred, however, especially for Pb a high voltage has to be applied. The best compromise was 20kV. At this voltage the depth of the analysed region in the film is $1.25\text{ }\mu\text{m}$. From measurements on the ceramic standards the following accuracy was obtained (atoms per formula unit): Mg ± 0.2 (due to high absorption correction), Fe ± 0.05 , In ± 0.02 . The estimated accuracy of Pb and Pt is ± 0.01 . All films were found to be Pb and Pt substituted $\text{MgFe}_{2-x}\text{In}_x\text{O}_4$, with $x = 0.09 - 0.11$. As shown in Fig. 7 the Pt content is about 0.05, with slightly increasing concentration at lower growth temperatures. The Pb content is strongly dependent on the growth parameters. At the lowest growth temperatures the concentration increases to about 0.2 atoms per formula unit.

So far we have analysed the composition of our films normal to the plane of the platelet with an analysed depth of $1.25\text{ }\mu\text{m}$. In order to study the composition as function of film thickness we have grown a $27\text{ }\mu\text{m}$ thick film (60 min, 125 rpm, 760°C). Analysis are performed on the broken and polished platelet normal to the growth direction with steps of $2.8\text{ }\mu\text{m}$ from substrate to film surface.

FIG. 7

Analysed Pt and Pb content in the films vs growth temperature. Open symbols, vertically dipped; full symbols, horizontally dipped with substrate rotation 125 rpm; dipping time min.

FIG. 8

Concentration vs depth in a $27\text{ }\mu\text{m}$ thick film, horizontally dipped with substrate rotation 125 rpm for 60 min. at 760°C .

As can be seen from Fig. 8 the Pb and In contents decrease when going to the film surface while the Pt content slightly increases. These compositional variations are probably related to changes in growth with dipping time.

Magnetic parameters

The saturation magnetization of the films was measured with a vibrating sample magnetometer. The $4\pi M_s$ values decrease continuously from 2000 ± 100 Gauss for a film grown at 790°C to 1300 Gauss for a film grown at 724°C . Rotation of the substrate leads to about 10% lower values of $4\pi M_s$. Magnetic torque measurements revealed that the easy axes of magnetization are in-plane. In accordance with this result no stripe domains were observed.

Discussion

We have seen that a rather high supersaturation of the flux ($\Delta T \sim 200^\circ\text{C}$) is necessary to obtain film growth on (100)-syton polished MgO substrates. An explanation can be found in the higher surface free energy of a (100)-plane of MgO compared to a (111)-plane. Film growth on (111)-MgO starts about 100°C higher than on (100)-MgO substrates (19), so when an insufficiently polished (100) substrate is dipped at a temperature between these saturation temperatures, initial growth can occur on those parts of the surface which have a lower surface free energy (20). This explains why growth on diamond polished substrates starts at a higher temperature than on syton polished substrates. As a result films on diamond polished substrates have an inferior quality and <100> directions of film and substrate can even make a small angle with each other.

We find an appreciable drop of the saturation magnetization with decreasing growth temperature. This effect can be attributed to the increasing Pb concentration. The lead ions are probably substituted at octahedral sites, which gives a decrease of $4\pi M_s$. At the same time the Curie temperature decreases due to the decreasing magnetic interaction and this leads to a further lowering of the magnetization. The influence of Pb is clearly proved by the effect of substrate rotation. Finally the equilibrium distribution of Mg ions also depends on the temperature. At lower temperatures more Mg is present at octahedral sites, and this also contributes to the lowering of $4\pi M_s$. So far we did not succeed in growing films with the preferred magnetization direction perpendicular to the film plane. This is probably due to the compressive stress in combination with a negative magnetostriction constant λ_{100} of the ferrite. Assuming Young's modulus $E \sim 2 \times 10^{12}$ dyn/cm², a misfit $\Delta a = -0.02$ Å corresponds to a stress $\sigma \sim -6 \times 10^9$ dyn/cm². If we further take $4\pi M_s \sim 1500$ G and $\lambda_{100} \sim -10^{-5}$, the stressinduced anisotropy field is $H_{\text{stress}} \sim -1500$ Oe. According to Borrelli (8) the growth-induced anisotropy in bulk crystals is of the order $H_{\text{growth}} \sim +1000$ Oe. If H_{growth} has a similar magnitude in the films a slightly positive misfit is necessary. We have tried to achieve this by adding small amounts of either Al_2O_3 or Ga_2O_3 to the flux. However, the resulting films always showed light colored, broad, straight lines along <100> directions as soon as $\Delta a > -0.014$. This means that due to the occurrence of some stress

relieving mechanism no perfect films could be grown with $\Delta a > +0.003$ at the growth temperature.

Conclusions

We have shown that it is possible to grow epitaxial films of magnesium-indiumferrite on (100) MgO substrates by means of the LPE method. To grow perfect films a good surface finish of the substrates is necessary. A serious disadvantage of MgO is the large difference in thermal expansion compared with the ferrite. As a consequence good films are always in compression at room temperature.

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