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LIQUID PHASE EPITAXIAL GROWTH OF COPPER FERRITE FILMS

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ABSTRACT

Single crystal CuFe$_2$O$_4$ films were grown by the LPE method from a PbO-B$_2$O$_3$ flux on (100), (110) and (111) MgO substrates. Smooth films were obtained only on the (111) substrate orientation. Temperature and time dependence of the growth are described. By means of the Bitter method serpentine like domain structures can be observed. Evidence is presented for the connection between domain structure and tetragonal distortion of the epitaxial layer.

INTRODUCTION

Epitaxially grown spinel ferrite films supporting bubble domains so far have only been grown by CVD methods [1]. Recently LPE growth of spinel films with good quality has been reported [2,3]. Though studies of single crystals indicated the presence of a growth induced uniaxial anisotropy in cubic spinel ferrites [4], attempts to grow LPE films with uniaxial anisotropy were unsuccessful. Herman [5] has shown that copper ferrite in the tetragonal phase is a good candidate in this respect.

FILM GROWTH

We have grown epitaxial thin CuFe$_2$O$_4$ layers on MgO substrates, which were cut within 0.5° of the desired plane from an x-ray orientated boule. Films were grown by vertical dipping of syton polished substrates in a supersaturated melt of composition 1PbO, 0.25B$_2$O$_3$, 0.08CuO + 0.20CuFe$_2$O$_4$ (moles). The excess CuO is needed in order to ensure that CuFe$_2$O$_4$ is the primary crystallization phase; PbFe$_{12}O_{19}$ crystallizes if the excess CuO is lower than 30 %, while an excess exceeding to 80 % causes CuO to crystallize.

With this melt LPE films can be grown within the temperature range of 850-900°C, which is much higher than the cubic-tetragonal transition temperature (about 400°C) so that a good structural fit between the cubic spinel film and the MgO substrate is to be expected at the growth temperature.

Three substrate orientations, (100), (110) and (111) were used; however, smooth epitaxial films were obtained on (111) substrates only. Due to the misorientation (< 0.5°) of the (111) substrates small terraces could be observed on the surface of the films. Films grown epitaxially on (100) and (110) substrates were rough with surfaces consisting respectively of pyramids and ridges (Fig. 1) composed of (111) facets. Obviously only LPE growth on the habit spinel face (111) results in a smooth surface. In view of this result we have restricted our efforts to (111) substrates.

For a given value of the supersaturation (10-40°C) and for dipping times larger than 1 min. CuFe$_2$O$_4$ grows linearly with time. For shorter times the growth rate is higher while the film lattice constant is larger indicating the growth of a transient layer (Fig. 2).

The relation between growth-temperature, growth-rate, misfit and $\Theta_{\text{M}}$ is shown in Fig. 3. The average film composition, as determined from electron-micro-probe analysis, is Cu$_{0.87}$Fe$_{2.07}$Pb$_{0.06}$O$_4$ with an accuracy of about 0.03 pro atom pro formula unit. For the eight analysed films deviations of the Cu and Fe contents from the reported average value are within the limit of accuracy.

The Pb content increases slowly with increasing supersaturation from 0.03 at 874°C to 0.08 atoms pro formula unit at 856°C.
Fig. 3. Growth-rate (solid line) and misfit (dashed line) as a function of growth temperature. The numbers indicate 4 nMₘ values in Gauss. Dipping time 10 min.

DOMINO STRUKTUR

Serpentine like domain structures with a stripe period of 2-4 μm could be observed using the Bitter technique, revealing domain boundaries (Fig. 4). When a magnetic field is applied perpendicular to the plane of the platelet the domain width can be increased with increasing field, but above about 600 Oe, because of the vanishing contrast, the structure can not be observed anymore.

Torque measurements revealed negative overall Ku values (Kₜ excluded from Kᵤ); this has to be attributed to both the high value of the demagnetization energy and the negative sign of the misfit induced anisotropy. (Using λ₁₁₁ = 1x10⁻³ [6], E = 1.5x10¹² dynes.cm⁻² [7], aₜ - aₘ = + 0.02 R and assuming υ = 0.25 one finds Kₛₘ = -3/2 λ₁₁₁σ = -7x10⁶ erg/cm³).

From these data we see that a misfit induced anisotropy cannot be used as an explanation for the observed domain structure. To investigate whether a growth induced anisotropy is present we have annealed the films at different temperatures. Even after annealing for 24 hours at 1250°C no change in the domain pattern could be observed so that a growth induced anisotropy can almost be excluded.

A possible explanation of the domain structure of the films is a tetragonal distortion of the epitaxial layer. Up to now from x-ray analysis no evidence for this distortion could be found. The film on the substrate (texture goniometer method) as well as the film removed from the substrate (Guiner method) were found to be cubic.

Some support for a tetragonal tendency of the films is obtained from the anisotropy data. We have found a difference between the overall anisotropy (Kᵤ*) and the sum of the demagnetization (2 nMₘ) and misfit (Kₛₘ) contributions.

In Table I some illustrating values are reported.

<table>
<thead>
<tr>
<th></th>
<th>Kᵤ*</th>
<th>2 nMₘ</th>
<th>Kₛₘ</th>
<th>Ku</th>
</tr>
</thead>
<tbody>
<tr>
<td>As grown</td>
<td>-2.06</td>
<td>+1.75</td>
<td>-0.76</td>
<td>+0.45</td>
</tr>
<tr>
<td>As grown</td>
<td>-2.66</td>
<td>+3.23</td>
<td>-0.77</td>
<td>+1.34</td>
</tr>
<tr>
<td>Quenched from 860°C</td>
<td>-1.58</td>
<td>+0.96</td>
<td>-0.76</td>
<td>+0.14</td>
</tr>
<tr>
<td>Cooled from 860°C</td>
<td>-1.95</td>
<td>+3.82</td>
<td>-0.68</td>
<td>+2.55</td>
</tr>
</tbody>
</table>

When taking Ku = Kᵤ* + 2 nMₘ - Kₛₘ it follows that Ku is positive; however, there is a large uncertainty due to the inaccuracy of 2 nMₘ of about 4x10⁴ erg/cm³. The highest Ku values are obtained for the slowest cooling rate. Such a behaviour would be consistent with the presence of a stress due to the fact that the film tends to become tetragonal.

For comparison we have studied the relation between domain pattern and tetragonality on bulk copper ferrite single crystals grown from the same melt as the films.

Fig. 4. Bitter domain pattern on a 4.8 μm thick copper ferrite film grown at 859°C.

Fig. 5. Bitter domain pattern on a (111) facet of an as grown copper ferrite single crystal.
On the (111) facets of as grown single crystals only a few isolated areas with a domain pattern (Fig. 5) can be made visible with the Bitter technique and no deviations from cubic symmetry are found from x-ray analysis.

Fig. 6. Bitter domain pattern, running in three directions, observed on a tetragonal copper ferrite (111) facet. The facet orientation is drawn in the inset.

However, when these crystals are quenched from 800°C to room temperature no domain patterns are observable anymore.

On the other hand, when the crystals are slowly cooled through the cubic-tetragonal transition temperature they become tetragonal and a very pronounced domain pattern, resembling that of the films, can be observed; but, also large areas with parallel domain boundaries are observed. Three directions with angles of about 120° to each other are present (Fig. 6). When those three directions are considered to be the projections of the cubic <100> directions on the (111) film surface, the areas with parallel domain boundaries are single crystalline tetragonal areas with a distinct [100] direction being the tetragonal C-direction.

In view of these results we believe that the serpentine like domain patterns observed on the films can be explained by assuming a slight tetragonal distortion of the CuFe₂O₄ layer with the three <100> directions having an equal chance to become c-direction, resulting in a random distribution among the three possibilities.

An other connection between domain structure and tetragonality is found in Al-substituted copper ferrite films. Bulk CuFe₂₋ₓAlₓO₄ with x values above 0.30 can not be obtained in the tetragonal phase by slow cooling. This is in agreement with the observation that the domain structure in Al-substituted CuFe₂O₄ film vanishes for x > 0.30. Details concerning this subject will be published separately.

CONCLUSIONS

We have shown that smooth epitaxial copper ferrite films can be grown by the LPE method on (111) MgO substrates. Torque measurements yielded positiv Ku values after correction for demagnetization and for misfit induced anisotropy. In view of the domain behaviour in the presence of an external magnetic field there must be a component of the magnetization perpendicular to the epitaxial layer. The domain pattern can not be explained by a misfit induced or by a growth induced anisotropy. From the results of our experiments we believe that the observed domain structure is caused by a tendency of the layer to become tetragonal.

REFERENCES