MAGNETIC ANISOTROPY AND DOMAIN STRUCTURE OF MANGANESE FERRITE GROWN EPITAXIALLY ON MgO*

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INTRODUCTION

The properties of polycrystalline manganese ferrite thin films have been discussed in previous papers^{1,2}. The present study was undertaken to obtain supplementary information on the magnetic anisotropy and domain properties of the films. The ferrite films were grown epitaxially by an evaporation process. An advantage of working with single-crystalline ferrite films is that studies of the domain structure are simplified. Furthermore, the magnetic anisotropy is not reduced to the average of the randomly oriented crystallites.

Epitaxial growth occurs on solids with equal or related crystal structures and types of chemical bonding, having at least one crystal face of comparable structure. Well-known substrates for spinel ferrites are MgO for many orientations and sapphire (Al_2O_3) with its (001) face fitting the (111) face of the spinel.

In the present investigation monocrystalline MgO, with a lattice parameter of 4.21 Å, was chosen as substrate. For manganese ferrite of ideal stoichiometry lattice parameters up to 8.50 Å have been found^{1,3,4}. For the ferrite investigated, however, the fit between the lattices was not so exact. This meant that the misfit led to a compressive force in the ferrite lattice. The compression, however, was partly compensated by the occurrence of dislocations.

In the special combination of MnFe_2O_4 and MgO the coefficients of thermal expansion are practically equal ($12 \times 10^{-6} \text{ mm } ^\circ\text{C}^{-1}$), so that during cooling after the evaporation process little or no change in strain occurs. The strain introduced by the misfit is therefore the main source of influence, through magnetostriction, on the magnetic anisotropy.

PREPARATION AND STRUCTURE

The films were prepared by the reactive evaporation of metal oxides as described by Hulscher *et al.*¹ for polycrystalline manganese ferrite films. During evaporation an oxygen partial pressure of about 10^{-4} Torr was present. The source materials (pressed and sintered MnO and Fe_2O_3 powders) were evaporated by heating with an electron gun. From polarographic analysis of the evaporated film the ratio Mn:Fe

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was found to be 0.95 : 2.05. The evaporation speed was approximately $2 \text{ \AA s}^{-1}$. The substrate temperature could be varied from 30° to 600°C . For magnetic measurements films with a thickness of $2500 \text{ \AA}$ were prepared and for investigation with the electron microscope the thickness was $500\text{--}1500 \text{ \AA}$.

To prepare defect-free MgO surfaces several methods were tried. The best monocrystalline ferrite films with relatively few defects were obtained by evaporation onto a polished (100) plane etched in 85% H_3PO_4 at 150°C for 15 s.

At lower substrate temperatures the initial products were microcrystalline in nature, *i.e.* they did not exhibit epitaxial growth. Large monocrystalline areas with the correct (100) orientation subsequently recrystallized out when annealing was carried out for 5 h at 780°C . The process is assumed to be epitaxial recrystallization, with the possibility of chemical reaction with the MgO substrate not excluded. Optimal results were obtained after evaporation onto substrates at 400°C . The effects of recrystallization could be seen in the changed diffraction pattern, in the improved adherence between film and substrate, and in squarer hysteresis loops and lower coercive field strengths.

The structure of the evaporated and recrystallized films was studied with the transmission electron microscope. For this purpose it was essential that the ferrite film be separated from the MgO substrate. A direct result of this treatment can be that the tensions are basically changed when the film is removed from the substrate. For separating, the film and substrate were placed in an almost saturated solution of magnesium citrate in water. The substrate material at the separation face dissolved slowly through pores in the film. The separation time depended on the quality of the film and could be more than a week.

Fig. 1. Electron micrographs of a (100)-oriented manganese ferrite film: (a) electron diffraction pattern; (b) Lorentz image obtained after a.c. demagnetization, exhibiting a chessboard domain pattern.

After recrystallization, all (100) oriented and epitaxially grown manganese ferrite films exhibit a monocrystalline diffraction pattern similar to that shown in Fig. 1(a). At first sight this agrees with the well-known spinel structure but with lengthy exposure times extra reflections of weak intensity become visible near the centre, between the spots of the (100) oriented f.c.c. lattice. Such extra reflections were also seen in our polycrystalline films¹, but they can now be indexed exactly as $(\bar{2}00, \bar{4}\bar{2}0, \bar{6}00)$. These reflections are not caused by double diffraction since in that case the indices would correspond to values obtained by the addition or subtraction of the indices of the basic pattern. The explanation that these (extra) reflections are formed by ordering of ions on the octahedral positions^{5,6} can be rejected on two grounds:

(1) MnFe_2O_4 is nearly a normal spinel⁷ and

(2) ordering between M_1^{2+} and M_2^{3+} ions is very improbable at higher temperatures.

Our findings support the explanation given by Grimes⁸ that the cause is a slight displacement of the metal ions in the octahedral sites along the [111] direction. According to this explanation, the spinel structure would fit the $F\bar{4}3m$ space group rather than the normally accepted $Fd\bar{3}m$ group.

The lattice parameter, which can be determined from the diffraction pattern, is 8.45 Å.

MAGNETIC MEASUREMENTS

The hysteresis loops for different films were measured using a vibrating sample magnetometer. In Fig. 2 films as-evaporated onto MgO and onto glass substrates are compared with an annealed film on MgO . No preferential direction of magnetization was found for the as-evaporated films. The annealed film on MgO , on the other hand, showed a preferential direction [110] with $H_c = 10 \times 10^4 \text{ A m}^{-1}$ and a hard direction [100], $H_c = 7 \times 10^4 \text{ A m}^{-1}$. For this film $J_s = 0.2 \text{ Wb m}^{-2}$.

In bulk crystals of MnFe_2O_4 the preferential direction is [111]. For thin films with orientation (100) the best fitting direction for magnetic preference is [110]. The [100] direction in the film as a hard direction is of course the same as in the bulk. The ratio of $\sqrt{2}$ for the two H_c values exactly fits the model of Kondorski⁹ for magnetic reversal by means of wall movement.

Domain pattern and wall movement under the influence of a magnetic field can be made visible with an electron microscope with a Lorentz attachment. With this accessory, d.c. or a.c. fields of maximum 8000 A m^{-1} can be applied in directions in the plane of the films. The observations of domains and domain walls are in accordance with the magnetic measurements. Because all films on MgO are (100) oriented with [110] as the preferential direction and [100] as the hard direction, domain magnetization can only be expected along the preferential axes, i.e. [110] and $[1\bar{1}0]$ with 90° and 180° walls. The domains can be generated by de-magnetization with a decreasing a.c. field along the hard axis.

The walls can be moved under the influence of the field of the Lorentz coils. When the field is gradually increased, the walls jump to new stable positions until

Fig. 2. Hysteresis loops of evaporated $Mn_{0.95}Fe_{2.05}O_{4+\gamma}$ films measured with a vibrating sample magnetometer: no preferential direction is shown on the as-evaporated film on (a) a glass substrate and (b) a (100) MgO substrate; (c), (d) the annealed film on (100) MgO measured in (c) the [110] preferential direction and (d) the [100] hard direction.

total magnetic reversal has taken place. The strength of the field at which reversal takes place varies from one position to another in the film. The minimum field was about $2400 A m^{-1}$. There were also areas which needed fields above $8000 A m^{-1}$.

Domains sometimes appear when a gradually increasing counter-field in the hard direction is applied to a completely magnetized film.

If the field is generated along the preferential axis magnetic reversal takes place without wall movement or formation of walls being observable.

A typical pattern resulting from demagnetization with an alternating field along the hard axis is the so-called chessboard pattern. This pattern (see Fig. 1(b)) consists entirely of 90° walls. Patterns with 90° and 180° walls were also observed.

The opportunities for observing domain walls are improved when the number of visible defects is larger. The defects hamper the movement of the domain walls, retarding the magnetic reversal and resulting in a greater coercive field strength¹⁰. Wall movements are slowed down at places where defects occur and sometimes the walls are fixed in one place.

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