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Structure and soft magnetic properties of sputter deposited MnZn-ferrite films

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In this paper we report the soft magnetic properties of thin films of sputtered MnZn ferrite deposited on thermally oxidized Si substrates. A high deposition temperature, 600 °C, together with the addition of water vapor to the sputtering gas was found to improve the initial ac permeability, μ. The highest value obtained was approximately 30. For MnZn-ferrite films with much larger grain sizes, as obtained by deposition on a polycrystalline Zn-ferrite substrate, a μ of 100 was obtained. The results are discussed in terms of the so-called nonmagnetic grain boundary model. © *1998 American Institute of Physics.* [S0021-8979(98)53211-2]

I. INTRODUCTION

The growth of thin layers of magnetically soft ferrites such as MnZn or NiZn ferrite has been studied recently by various groups.[1–3] This interest is motivated by potential applications such as magnetic thin-film read heads,[4] cladding layers for thin film inductors,[5] and microwave acoustic devices.[2] For most applications, two of the most important parameters are the resistivity of the layer and the ac permeability, μ. While the resistivity is similar to that of the bulk the permeability of the thin ferrite films, on which many authors do not report explicitly, appears to be significantly less. This may be deduced from previously published M vs H loops[2] where, even when grown epitaxially, the films lack the true softness which characterizes the bulk material.

It has been shown by other authors that the addition of oxygen during deposition can have the effect of improving the softness of a thin film MnZn ferrite.[1] We however, found that this can easily lead to an undesired oxygen rich ferrite. In the case of Fe_3O_4 it was found that the exact oxidation state of sputtered films could be more accurately controlled using H_2O.[6] In this paper we report the effects on the soft magnetic properties of MnZn ferrite when a small amount of water vapor is added to the sputtering gas.

II. EXPERIMENT

The films were deposited in a Perkin Elmer 2400-8L rf diode sputter system, using Ar at a constant pressure of 0.29 Pa (2.2 mTorr). The background pressure was approximately 1.3×10^{-4} Pa. The substrate temperature during deposition was monitored by a thermocouple inserted into the substrate table and silver paste was used to ensure a good thermal contact. The films were sputtered from a 10 cm diameter $Mn_{0.51}Zn_{0.42}Fe_{2.03}O_4$ polycrystalline ferrite target which has a bulk μ of approximately 4000. The deposition rate was 0.2 μm/h, with a rf power of 250 W, and the films, which were grown on Si substrates with a 0.5 μm pregrown thermal SiO_2 layer, were approximately 0.9 μm thick. The initial ac permeability was measured[7] using an HP4129A analyzer with an applied ac field of 2.5 A/m.

III. MAGNETIC PROPERTIES

The magnetic properties were studied as a function of two deposition parameters: additional water vapor in the sputtering chamber and substrate temperature. The effect of the presence of an additional amount of water vapor on the soft magnetic properties is shown, for three different substrate temperatures, T_s, in Figs. 1(a)–1(c). In the case of no additional added water vapor, [$p(H_2O)=1.3\times10^{-4}$ Pa] an increase in T_s does have an effect on μ, though the maximum value attained was only 16. Upon increasing $p(H_2O)$ the coercivity H_c [Fig. 1(a)] is reduced, and for a T_s of 550 or 600 °C H_c is approximately 1.6 kA/m with the addition of 0.13 Pa of H_2O. For $T_s=500$ °C the minimum H_c is approximately 2.8 kA/m.

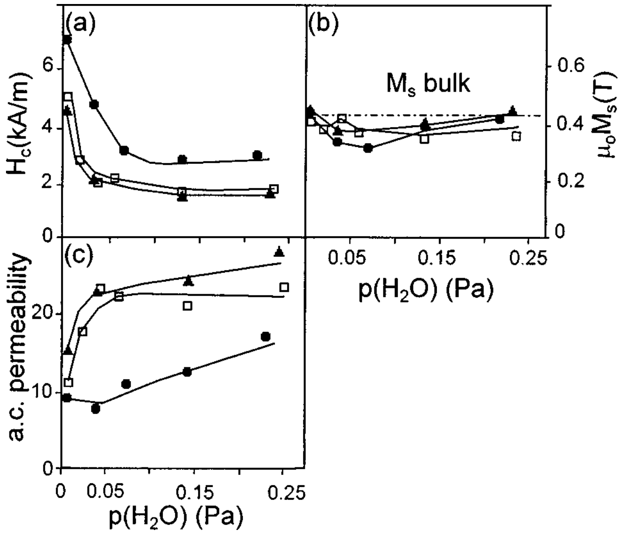

FIG. 1. The effect of the partial water-vapor pressure during sputtering on (a) the coercive field, (b) the saturation magnetization, and (c) the ac permeability of thin ferrite films. Deposited at 500 °C (circles), 550 °C (squares), and 600 °C (triangles).

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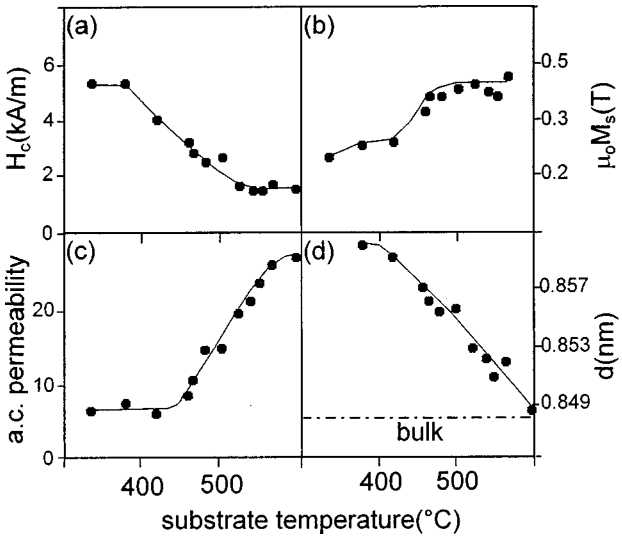

FIG. 2. The effect of a variation in substrate temperature at $p(H_2O)=0.13$ Pa on (a) the coercive field, (b) the saturation magnetization, (c) the ac permeability, and (d) the lattice parameter of a 0.9 μm MnZn-ferrite film.

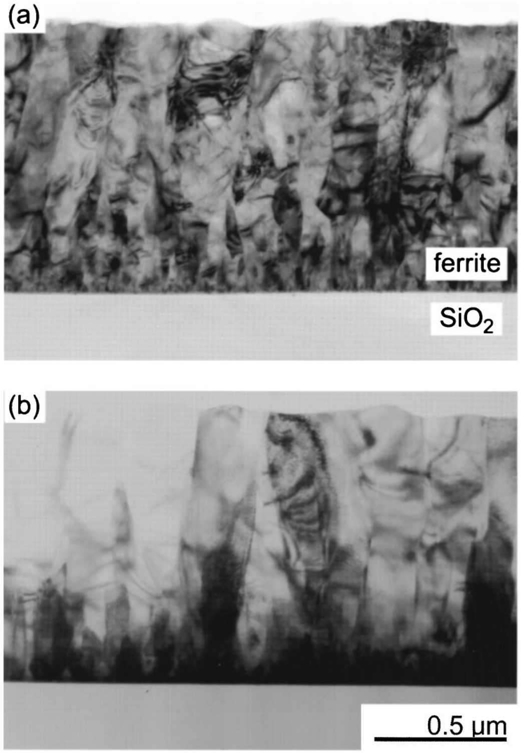

FIG. 3. TEM cross sections of films deposited at (a) 523 °C and (b) 604 °C.

The room temperature saturation magnetization, $\mu_0 M_s$, of the sputtered films, Fig. 1(b), is only slightly lower than that of the bulk material (0.44 T).

The ac permeability did not show any rolloff in the 1–13 MHz frequency range and the average value of permeability over this frequency range is what is given in Fig. 1(c). For the different T_s the trend is similar: an increasing $p(H_2O)$ leads to a higher μ, with the maximum, $\mu \approx 27$, being achieved with a T_s of 600 °C and a $p(H_2O)$ of 0.23 Pa.

While the trends in magnetic properties are independent of T_s the actual values of H_c and μ are not. The magnetic and structural properties (Sec. IV) of the sputtered ferrite were therefore measured for a new series of films where T_s was varied while holding the $p(H_2O)$ constant at 0.13 Pa. Figure 2(a) shows the influence of temperature on H_c which falls to approximately 1.4 kA/m for T_s higher than 560 °C. An increase in T_s also leads to an increase in the $\mu_0 M_s$, Fig. 2(b). Substrate temperatures which are less than 450 °C, result in a μ below 10, Fig. 2(c). Above 450 °C μ increases rapidly with increasing temperature and at 600 °C μ is approximately 27.

IV. STRUCTURAL PROPERTIES

The structural properties of the ferrite were also studied both as a function of $p(H_2O)$ and T_s. The width and position of the strongest peak, (400), in the θ–2θ Cu $K\alpha$ x-ray spectra did not show any relation to $p(H_2O)$ (while T_s was fixed). The stoichiometry of these films, together with those deposited with various substrate temperatures, was checked using x-ray fluorescence, XRF, and electron probe microanalysis, EPMA. For depositions at T_s less than 500 °C the composition did not appear to be influenced by $p(H_2O)$ and was, within experimental error, the same as the target material. For depositions at higher T_s films showed Zn deficiency if deposited without H_2O. The fact that this did not occur in the presence of H_2O may be due to the oxidation of metallic Zn on the surface of the film which would slow down any evaporation. For films with a reasonably high μ, such as those deposited at 550 °C/0.13 Pa water vapor, the stoichiometry was, within experimental error, the same as the target.

From the (400) x-ray diffraction peak positions the lattice parameter perpendicular to the film was determined for films deposited at different T_s, Fig. 2(d). The bulk (target) lattice parameter was 0.848 nm. These experiments, as well as x-ray measurements with a varying direction of the scattering vector and mechanical stress measurements, reveal a reduction in stress for increasing T_s. Due to the strain present in the ferrite films it is not possible to accurately determine the average crystal size via the analysis of x-ray peak widths. This was therefore determined via transmission electron microscopy (TEM) cross sections for films deposited at $T_s=523$, 565, and 604 °C. [The cross sections shown here are only for films deposited at 523 and 604 °C (Figs. 3(a) and 3(b), respectively).] While it is possible to discern a columnar structure within all the films it is clear that for a higher deposition temperature the columnar structure is more clearly defined. For the film deposited at $T_s=523$ °C there exist imperfections throughout the whole thickness of the film. This is in contrast to films deposited at a higher T_s where the formation of small crystallites only occurs during the initial stage of growth. In the later stages of growth a very distinct columnar structure appears. From the TEM cross sections the estimated average grain sizes for the depositions at 523, 565, and 604 °C were 90, 110, and 175 nm, respectively.

V. FILMS GROWN ON A Zn-FERRITE SUBSTRATE

In Sec. IV the values for the approximate grain size of the ferrite films, as determined through TEM, were reported.

From the nonmagnetic grain boundary model[8] (NMGB model) the relationship between the effective initial permeability, μ_e, the average grain size, D, and the intrinsic permeability, μ_i, of the ferrite within a grain is given by

$$\mu_e=\frac{\mu_i D}{\mu_i \delta+D}, \tag{1}$$

where δ is the width of the nonmagnetic grain boundary zone. Equation (1) implies that that for fixed values of δ and μ_i, μ_e can be increased by increasing the grain size. We therefore increased the in-plane grain size of the MnZn-ferrite films by growing on a mechanically polished polycrystalline Zn-ferrite ($ZnFe_2O_4$) substrate with a grain size of approximately 15 μm. Since the lattice parameter mismatch is less than 0.5% and the thermal expansion coefficients are similar,[9] Zn ferrite is an ideal substrate on which to grow MnZn ferrite. On account of the substrate being paramagnetic at room temperature the magnetic properties of a MnZn-ferrite film can be measured without a contribution from the substrate. Figure 4 shows a scanning electron microscope photograph of a 0.9 μm thick MnZn-ferrite film, deposited with $p(H_2O)=0.13$ Pa and $T_s=560\,°C$. As can be seen the in-plane grain size is around 15 μm. The film had a H_c of less than 0.1 kA/m and was therefore much softer than those deposited on the Si/SiO_2 substrates ($H_c\approx 1.4$ kA/m for films deposited under identical conditions on Si/SiO_2). The ac permeability of the films deposited on Zn ferrite was 100 ± 5.

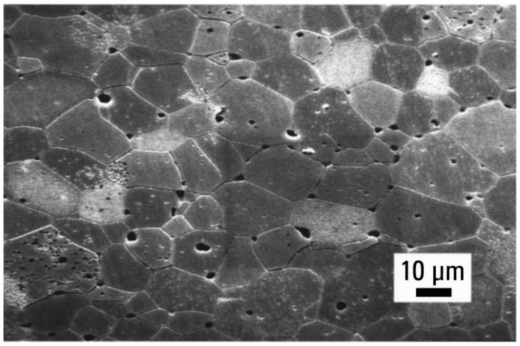

FIG. 4. SEM photograph of 0.9 μm MnZn-ferrite film deposited on a Zn-ferrite substrate.

VI. DISCUSSION AND CONCLUSIONS

The improvement in soft magnetic properties by adding water vapor to the sputtering gas was an unexpected result, for which we do not yet have an explanation. We did, however, consider the possibility that the presence of H_2O affects the oxidation state of either the Fe or Mn ions in the ferrite. Using a wet chemical technique it was found that the fraction of Fe^{2+} and Mn^{3+} ions in the films, with and without water vapor, were very similar to that of the target. It could, however, still be possible that the concentration of either Fe^{2+} or Mn^{3+} ions at the grain boundaries is not as in the bulk material and, since these ions can give rise to a large single ion anisotropy in the presence of a crystal field, this could result in grain boundaries with a high anisotropy. The effect of high anisotropy grain boundaries was considered by Pankert[10] and leads to a reduction in permeability.

The effect of the substrate temperature on the soft magnetic properties, which was also observed for films grown on the Zn ferrite, must be related to the increased mobility of the atoms when they arrive at the surface. This has the obvious effect of increasing the grain size which, according to the NMGB model, leads to a magnetically softer film. A higher temperature would also reduce the density of dislocations and other imperfections in the bulk of the grains and could reduce the thickness of the nonmagnetic grain boundary, thereby improving the softness of the ferrite.

The reduction in lattice parameter for increasing T_s, Fig. 2(d), is indicative of a lowering in the total stress which is present in these films (this was also checked using mechanical stress measurements). Taking the sign of the thermal mismatch between the substrate and the film into account such a behavior cannot be explained in terms of a thermal mismatch alone and there must exist excessive stress within the ferrite film itself. A shift in the lattice parameter, with respect to that of the bulk, is also observed for the MnZn-ferrite film deposited on Zn ferrite. A lowering of total stress for higher deposition temperatures may be responsible, at least in part, for the higher permeability achieved with these temperatures.

As would be expected from the NMGB model the choice of Zn ferrite as a substrate and the consequently larger grain size of the MnZn-ferrite film lead to a higher permeability. If, however, one substitutes into Eq. (1) the average grain size of the film shown in Fig. 4, together with a nonmagnetic grain-boundary thickness of a few nanometers (for the bulk a value of 1.4 nm has been determined[8]) then $\mu_i\approx\mu_e$, where μ_e has been found to be approximately 100. Such a low value of μ_i may be caused by the presence of residual stress in the films though it is important to realize that the cation distribution was not checked in these sputtered layers and that a deviation from the desired distribution could also result in a low μ.

A permeability of 30, as obtained for thin films on Si/SiO_2 is sufficient to utilize these layers as cladding layers for thin film inductors. As a flux guide material in yoke-type thin film read heads[4] a permeability of 30 is not quite sufficient. Further effort is therefore needed to realize a higher permeability and a lower deposition temperature.

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