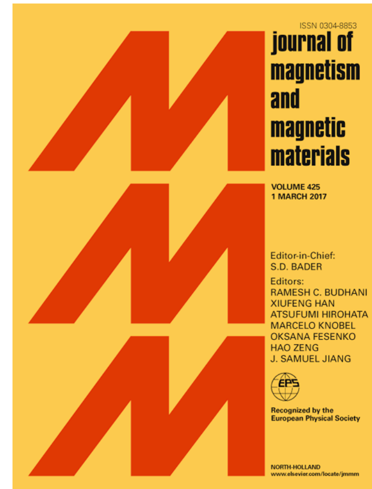

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Magnetic Properties of Superparamagnetic, Nanocrystalline Cobalt Ferrite Thin Films Deposited at Low Temperature

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Bulk cobalt ferrite, being a hard ferrite, shows high magnetization, high resistivity and high coercivity. If thin films of cobalt ferrite can be deposited at a low enough temperature and if its coercivity can be reduced, cobalt ferrite will make a very good candidate for use as a magnetic core of an integrated inductor in RF-CMOS ICs. Though polycrystalline and epitaxial thin films of cobalt ferrite have been made by various techniques, there are no reports of thin films of superparamagnetic cobalt ferrite. In this work, nanocrystalline cobalt ferrite thin films, which are superparamagnetic as deposited, have been prepared in the solution medium at ~190°C, using microwave irradiation. The as-prepared films have a saturation magnetization (M_S) of 401 emu/cc and coercivity (H_C) of 19 Oe at room temperature for a crystallite size of 2 nm. The cobalt ferrite powder obtained as a by-product during the same process has M_S of 50 emu/g and H_C of 5 Oe at room temperature, making it superparamagnetic. The as-prepared films were annealed in air at 300°C for 5 min and 10 min. Annealing for 10 min results in an increase in crystallite size to 36 nm, M_S increases from 401 emu/cc to 545 emu/cc, and H_C increases from 19 Oe to 860 Oe. The change in magnetic properties can be directly associated with change in the crystallite size and degree of crystallographic inversion, as determined by neutron diffraction and deduced from X-ray photoelectron spectroscopy.

Index Terms— **Cobalt ferrite, Ferrite thin Films, Magnetic materials, Superparamagnetism.**

I. Introduction

Magnetic thin films with high saturation magnetization (M_S) and low coercivity (H_C), as well as high resistivity, have become important for GHz RF-CMOS applications. Such films can be used as the magnetic core of integrated inductors in RF-CMOS ICs to enhance the inductor density and to render them capable of operating in the GHz regime [1]. Spinel ferrites satisfy the requirements of high magnetization and high resistivity, provided the deposition of thin films of such ferrites can be made compatible with today's CMOS back-end of the line processing, i.e., at a temperature not higher than about 400°C. Progress has recently been reported in this direction by demonstrating the performance of solution-processed thin films of nanocrystalline zinc ferrite [2], [3]. Being a normal spinel, bulk zinc ferrite is not ordinarily ferrimagnetic. But, if the crystallite size is made sufficiently small, zinc ferrite exhibits ferrimagnetic behavior [4]. An inverse spinel ferrite like cobalt ferrite, which has a large magnetisation, might be expected to be a better candidate than nanocrystalline, ferrimagnetic zinc ferrite.

Bulk cobalt ferrite has high permeability, high saturation magnetization (M_S), high electrical resistivity, high coercivity (H_C), and high magnetocrystalline anisotropy [5]. It is an inverse spinel ferrite, with inversion parameter ranging from 0.75 to 0.89 [6]. Concas et al. [6] have reported that the inversion parameter of cobalt ferrite depends on how it is synthesized, leading to different magnetic properties. Different factors, including site preference of cations based on crystallite size [7], the method of preparation, temperature of synthesis [8], and post-synthesis thermal treatment [9] influence how Co^{2+} and Fe^{3+} ions arrange themselves in the octahedral and tetrahedral sites of the spinel structure.

Although bulk cobalt ferrite has high M_S, it also has a high H_C, which would lead to hysteresis losses in high-frequency applications. Due to cubic anisotropy [10], cobalt ferrite has a high remnant magnetization (M_r), leading to a high M_r/M_S value of 0.83. Reduction in crystallite size reduces the volume (V) which, in turn, reduces the anisotropy energy (K_AV, where K_A is the anisotropy energy constant), which favours superparamagnetism [11]. Although there is a slight reduction in saturation magnetization above the blocking temperature, superparamagnetism (SPM) results in coercivity reducing to zero [12]. Different investigators have reported different particle sizes ranging between 5 nm and 22 nm for the onset of superparamagnetism [13]-[17].

Superparamagnetic cobalt ferrite powder has been synthesized using alkalide reduction [13], the sol-gel method [14], thermal decomposition [18], hydrothermal method [19], and solid-state co-precipitation reaction [20]. Komarneni et al. [21] showed how ferrites of fine crystallite size could be obtained rapidly through microwave-hydrothermal synthesis, though they were unable to obtain phase-pure cobalt ferrite powder. Caillot et al. [22] have also reported the synthesis of cobalt ferrite powder using the microwave-hydrothermal process; the final product had some impurities, but a high M_S and a high coercivity (1000 Oe).

Thin films of cobalt ferrite have been deposited using several deposition techniques. Avazpour et al. [23] used the sol-gel technique to spin-coat such films, followed by annealing at up to 650°C, obtaining M_S ranging from 176-237 emu/cc and a high coercivity (1.4 – 1.8 T). Pulsed laser deposition (PLD) [24], [25] has also been used to deposit cobalt ferrite thin films. Ragunathan et al. [24] found, in such films, $M_S \approx 275$ emu/cc and $H_C \approx 1800$ Oe, when the deposition temperature was 600°C. Tanaka et.al [26] used the evaporation technique in O_2 plasma to obtain cobalt ferrite films at 500°C, followed