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Preparation and characterization of ZnSn-substituted barium ferrite thin films

Darja Lisjak [a,*], Kristina Žužek Rožman [b], Federica Celegato [c], Elena Olivetti [c], Marco Coisson [c], Massimo Pasquale [c], Miha Drofenik [a,d]

[a] Department for Materials Synthesis, Jožef Stefan Institute, 1000 Ljubljana, Slovenia
[b] Department for Nanostructured Materials, Jožef Stefan Institute, 1000 Ljubljana, Slovenia
[c] INRIM, Electromagnetics Division, 10135 Turin, Italy
[d] Faculty for Chemistry and Chemical Engineering, University of Maribor, 2000 Maribor, Slovenia

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ABSTRACT

The preparation of ZnSn-substituted barium ferrite films by sputtering deposition was studied. The as-sputtered films were amorphous, and annealing at a minimum of 750 °C was required to crystallize the films, based on the X-ray diffraction analysis and the magnetic measurements. Scanning electron microscopy combined with energy-dispersive X-ray spectroscopic microanalysis confirmed that the films were single phase with the composition $BaZn_xSn_xFe_{12-2x}O_{19}$, $x=0.2-0.3$, and their thicknesses were 0.4–1.0 μm when annealed at 750–900 °C. Atomic and magnetic force microscopy studies showed no significant grain growth upon annealing and that the films consisted of single-domain grains forming interaction-cluster-type domains. The natural ferromagnetic resonance frequency was determined at around 4 GHz, together with substantial magnetic losses that make these films promising candidates for microwave absorbers.

1. Introduction

Barium ferrite ($BaFe_{12}O_{19}$) is a well-known compound suitable for hard magnetic, magnetic recording, magneto-optic and high-frequency applications. Its high magnetocrystalline anisotropy originates from its highly anisotropic crystal structure, where the Fe ions occupy five crystallographic sites. If the Fe is substituted with, for example, Zn and Sn ions ($BaZn_xSn_xFe_{12-2x}O_{19}$), the magnetic anisotropy can be decreased to such an extent that the uniaxial anisotropy changes to planar at $x>1.6$ [1] and shows a typical soft-magnetic behavior. At the same time, the application frequency can be tuned, by increasing the value of x, to well below 48 GHz [2]. For their various applications, ferrites are used in the form of bulk ceramics, powders or as films.

The sputtering process has been applied previously for the preparation of $BaFe_{12}O_{19}$ films [3–9], but there are very scarce data on the use of this technique for the preparation of the more complex barium ferrite systems [6], such as $BaMe^{II}_xMe^{IV}_xFe_{12-2x}O_{19}$, where Me^{II} and Me^{IV} are bi- and tetra-valent cations, respectively. Sputtering deposition offers many advantages over other thin-film deposition techniques, both for academic research and for industrial, large-scale production. These advantages include the following: the high purity of the deposited film, made possible by the high-vacuum/plasma environment; the absence of toxic processing gases and waste products; the opportunity to maintain the stoichiometry of the alloys and compounds (with the possible utilization of a partly reactive atmosphere); the possibility to cover large substrates with an excellent thickness uniformity; and the ability to cover a substrate with complex (concave/convex) shapes by conforming the target shape to that of the substrate.

The purpose of this investigation was to study the sputtering-deposition method for the preparation of chemically complex ZnSn-substituted barium ferrite films with the chemical composition $BaZn_xSn_xFe_{12-2x}O_{19}$, $x\leq 1$, which are suitable for microwave applications.

2. Materials and methods

Films with thicknesses of 0.4–1.0 μm were deposited at room temperature on silicon-nitride-covered Si wafers by RF sputtering, starting from a mosaic target made from sintered chips with the composition $BaZnSnFe_{10}O_{19}$. The base pressure of the chamber was 2×10^{-7} mbar and the Ar deposition pressure was 1×10^{-2} mbar. For the rf power used (200 W), the typical deposition rate was 2.1 Å/s. After this deposition the films were thermally

* Corresponding author. Tel.: +386 1 4773 872; fax: +386 1 2519 385.
E-mail address: darja.lisjak@ijs.si (D. Lisjak).

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annealed at 600–1000 °C for 3 h in air. In addition to this, one film was annealed at 700 °C for 70 h.

The films were characterized with X-ray diffraction (X'Pert PRO MPD Diffractometer PANalytical using $CuK_{\alpha 1}$ radiation) and with scanning electron microscopy (SEM, Jeol 5800) combined with a LINK-ISIS system for the energy-dispersive X-ray spectroscopy (EDXS) analyses.

The magnetic properties of the films were measured at room temperature with an alternating gradient-field magnetometer, with the magnetic field applied either in the sample plane or perpendicular to it, depending on the probe employed. The maximum field was equal to 1.8 T, and a background subtraction of the sample holder and the substrate was applied to all the measurements.

The evolution of the magnetic-domain structure was examined using a Digital Instruments Dimension 3100 atomic force microscope (AFM) with an MFM extender box for the phase-shift measurements. The topography scan was performed in tapping mode and the magnetic contrast was measured in an interleave scan with a lift height up to 280 nm. A commercial Si tip coated with a Co alloy, which was magnetized vertically, was used.

The microwave measurements were performed using a coplanar waveguide (CPW) connected to the ports of an Anritsu 37397C 40 MHz – 65 GHz Vector Network Analyzer (VNA). During the measurements the film samples were positioned face down on the CPW. A magnetic field up to about 0.5 T was applied parallel to the 200-μm-wide center conductor of the CPW using an electromagnet. The differential analysis of the amplitude and phase of the S_{21} scattering parameters measured with the VNA [10] allowed a determination of the evolution of the ferromagnetic resonance (FMR) frequency with the applied field. The FMR data were interpreted according to the Kittel equation for bulk geometry – i.e., linear with the applied field – due to the film thickness and the observed surface roughness.

3. Results and discussion

3.1. Crystallization of the films

The substrate temperature was not suitable for the direct preparation of crystalline barium ferrite films. As a result, none of the as-deposited films showed ferrimagnetic behavior, as was observed before for the basic $BaFe_{12}O_{19}$ composition [3–6,8,9]. In fact, after the subtraction of the contribution of the sample holder and of the substrate, only a very weak diamagnetic component was observable. Therefore, a thermal post-treatment was applied to the as-deposited films. According to the XRD analysis (Fig. 1) the crystallization of the barium ferrite started at 750 °C. The corresponding XRD pattern shows weak barium ferrite diffraction peaks and those of the substrate. In contrast the films annealed below 750 °C showed only the diffraction peaks of the substrate and a high background typical for amorphous compounds. The films did not crystallize even after annealing at 700 °C for 70 h. This clearly suggests that annealing above 700 °C is necessary for the crystallization of these $BaZn_xSn_xFe_{12-2x}O_{19}$ films. Indeed, most of the previous work [3–6,9] on the basic barium ferrite composition ($BaFe_{12}O_{19}$) reported that 800 °C was required for the crystallization to take place. The nucleation of barium ferrite crystals was observed at 700–800 °C by Sui and Kryder [9], which is in agreement with this study and with [8]. By increasing the firing temperature to above 750 °C the relative intensities of the barium ferrite peaks increased. An additional diffraction peak, corresponding to the cristobalite structure, can also be observed in the corresponding XRD patterns. This suggests that the substrate (silicon nitride layer) oxidized during annealing. No preferential orientation of the barium ferrite grains in the annealed films was observed with the XRD.

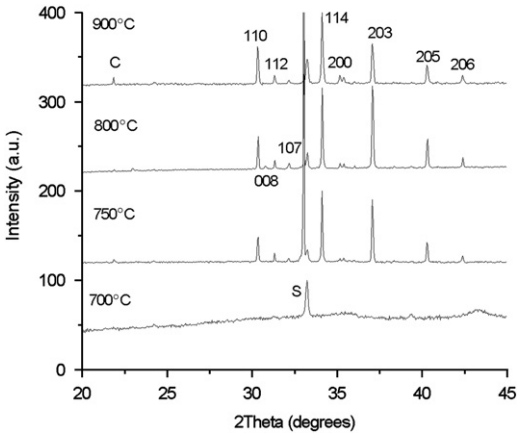

Fig. 1. XRD patterns of the films annealed for 3 h, where S denotes the substrate and C denotes the cristobalite. The barium ferrite peaks are indexed with the space group $P6_3/mmc$ (194).

The SEM investigation revealed that a cracking and delamination of the films occurred during annealing, and that this effect increased with the annealing temperature. This can be explained by the large mismatch in the linear thermal expansion coefficient between the barium ferrite (12 ppm/K for polycrystalline material [11]) and the silicon nitride substrate (3 ppm/K [12,13]), which induced such a large stress to the film/substrate interface that cracking and finally delamination were the result. The latter can also affect the oxidation of the substrate to SiO_2 (cristoballite—Fig. 1). It should be noted that the as-deposited films did not show any of these defects, due to the more flexible, amorphous nature of the film. Furthermore, with the EDXS analyses of the films, around 6 – 8 at% of Si was detected together with the Ba, Fe, Sn and Zn. Because of the low film thicknesses, the Si may originate from the substrate. However, previous studies reported on the chemical incompatibility of the barium ferrite and the Si [3,5–7] that may also be the origin of the Si in the film. In future studies another, e.g., sapphire, or an additional underlayer, e.g., $Gd_3Ga_5O_{12}$ or $ZnFe_2O_4$ [3,8], will be used to improve the film adhesion and to avoid chemical reactions between the film and the substrate during the annealing. The fraction of Sn and Zn ($BaZn_xSn_x$-$Fe_{12-2x}O_{19}$, x–0.2 – 0.3) was lower than in the target (BaZnSn-$Fe_{10}O_{19}$, $x=1$). Nevertheless, no additional phases were observed with backscattered electrons. Therefore, we can conclude that the loss of Zn and Sn occurred during the deposition.

3.2. Magnetic properties of the films

The magnetic properties of the films developed with the thermal treatment in the same way as observed before with the XRD. Magnetic hysteresis loops, typical for ferro/ferrimagnetic materials, were observed for the films annealed at a minimum of 750 °C (Fig. 2). All the films annealed at 750–900 °C show similar hysteresis loops, with coercivity values around 0.13–0.15 T. These values are only slightly higher than the 0.12 T measured previously on powders with the same nominal composition [14].

The hysteresis loops measured in-plane are relatively square and show much higher remanent magnetization values than those loops from the same samples measured out-of-plane. The out-of-plane loops showed similar coercivity values, but a significantly slower approach to saturation than those measured in-plane with a remanent-to-saturation magnetization ratio of 0.2–0.4. In both cases a precise estimation of the saturation magnetization cannot be provided, because at an applied field