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Ultra-high resistive and anisotropic CoPd–CaF_2 nanogranular soft magnetic films prepared by tandem-sputtering deposition

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ABSTRACT

Ultra-high resistive and anisotropic soft magnetic films for gigahertz applications are desirable to demonstrate the really practical films. Here we present a study of novel nanogranular films fabricated by tandem-sputtering deposition. Their electromagnetic properties and nanostructure have also been discussed. These films consisted of nanocrystallized CoPd alloy-granules and CaF_2 matrix, and a specimen having a composition of $(Co_{0.69}Pd_{0.31})_{52}$–$(Ca_{0.31}F_{0.69})_{48}$ exhibited distinct in-plane uniaxial anisotropy after uniaxial field annealing with granule growth. Its complex permeability spectra have a ferromagnetic resonance frequency extending to the Super-High-Frequency band due to its higher anisotropy field, and its frequency response was quite well reproduced by a numerical calculation based on the Landau–Lifshitz–Gilbert equation. Furthermore, it was clarified that the CaF_2-based nanogranular film exhibits a hundredfold higher electrical resistivity than conventional oxide or nitride-based films. Higher resistivity enables the film thickness to achieve a margin exceeding threefold against eddy current loss. The greater resistivity of nanogranular films is attributed to the wide energy bandgap and superior crystallinity of CaF_2 matrix.

1. Introduction

Miniaturization of magnetic devices, e.g., planar inductors, using magnetic thin films has been investigated in previous works [1–3]. Recently, advanced studies on integration of such miniaturized devices onto LSI packages are being conducted [4,5]. For low-loss excitation of magnetic devices in the GHz region, magnetic thin films having a high ferromagnetic resonance (FMR) frequency f_r, i.e., both high saturation magnetization M_s and anisotropy field H_k are desirable (Eq. (1) [6]; γ is the gyromagnetic ratio). Thicker magnetic films are also demanded to reduce the reluctance of the magnetic circuit and to increase device impedance but an increased thickness produces high eddy current loss decreasing of the quality factor of the devices. Ultra-high electrical resistivity is required to eliminate eddy current loss P_e as indicated in Eq. (2) [7], where k_e is the proportionality constant, t is the material thickness, f is the frequency, M_m is the maximum magnetization, and ρ is the electrical resistivity.

$$f_r = \frac{\gamma}{2\pi}\sqrt{M_s \cdot H_k} \tag{1}$$

$$P_e = k_e \cdot \frac{(t \cdot f \cdot M_m)^2}{\rho} \tag{2}$$

Additionally, samples should be prepared by a dry process such as sputtering for fabricating the LSI packages.

Utilizing the nanogranular materials is the most suitable solution for the above. Nanogranular materials have a nanostructure in which functional nanosized granules dispersed in a matrix material. In previous studies, the authors reported that nanogranular films, which consist of a magnetic metal for granules and an insulation ceramic for a matrix, exhibit unique properties such as tunnel magnetoresistance (TMR) [8,9], magnetoelectric effect [10], and ferromagnetic properties [11,12] based on the random anisotropy model [13]. Even if granules stand alone in the matrix, granular films exhibit ferromagnetic properties when the magnetic coupling between granules is maintained. However, isolation of the granules interrupts of the electrical percolation hence increasing ρ [14,15]. It was clarified that soft magnetic $(Co_{0.85}Pd_{0.15})_{71}$–$(a\text{-}Si_{0.21}O_{0.79})_{29}$ granular film exhibits both high saturation magnetization at around 0.8 T and a high anisotropy

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field at around 32 kA/m, hence a high static permeability of about 20 and a high FMR frequency above 3 GHz have been obtained in complex permeability spectra [12]. This film also exhibits high resistivity around 9 μΩ m. However, higher resistivity is required to obtain a thicker film for the GHz region, though this is several times higher resistivity than that of single-phase metallic amorphous films.

The authors found that the electrical resistivity increases extremely when oxide or nitride matrices were replaced with fluorides [8]. In nanogranular structure, conventional oxide or nitride matrices have an amorphous structure and nonstoichiometric composition, whereas fluorides often exhibit a polycrystalline structure [8]. Furthermore, fluorides are superior insulators in nanogranular systems because they are the widest energy bandgap materials among solids. However, very few studies have reported on fluoride-based soft magnetic nanogranular or nanoheteroamorphous [16] films [17–19]. We believe that higher anisotropy fields, higher resistivities, and lower Gilbert damping factors are necessary for GHz applications, though these studies achieved better films with high saturation magnetization.

In this study, the authors point out the importance of carefully selecting fluoride and sample preparation methods. Calcium fluoride (CaF_2) was selected as a matrix material for nanostructure because CaF_2 has both the wide bandgap (12.1 eV [20]) and the low solubility in water (0.16 mg/L at 293 K [21]). Additionally, the authors utilized rf tandem-sputtering deposition for sample preparation [8,9]. As mentioned below in detail, this method is a co-sputtering technique, and may enables us to obtain a phase-separated nanostructure of CaF_2-based nanogranular films compared with conventional diode-sputtering methods. As far as we know, this is the first worldwide report of fabricating nanogranular soft magnetic films by this technique. Here, the authors describe the electromagnetic properties and nanostructure of a novel nanogranular soft magnetic film consisting of CoPd alloy granules and CaF_2 matrix and having especially high-frequency permeability spectra, high electrical resistivity, and nanostructure dependence.

2. Materials and methods

A schematic view of an rf magnetron tandem-sputtering deposition system for preparing nanogranular film samples is presented in Fig. 1. The most striking feature of this equipment is that the sputtering target for granules and that for matrix are separate, and free radicals from each target are immiscible in the plasma. Target 1 is a fluoride matrix source consisting of polycrystalline CaF_2 disk; target 2 is a source for metallic granules consisting of Pd chips on a pure Co disk. Reagent-grade sputtering targets were prepared as raw materials. The vacuum chamber was cryopumped to under 4.0×10^{-5} Pa. Two plasmas were generated at the same time from each target when the gas pressure of pure Ar for plasma was maintained at 6.7×10^{-1} Pa. Mirror-polished glass with dimensions of $50 \times 50 \times 0.5$ mm^3 was used for a substrate. A substrate on the water-cooled anode (298 K) was rotated under the targets at a peripheral speed of 0.13 m/s, and a magnetic field of 25 kA/m was induced in the in-plane direction of the substrate using a pair of NdFeB permanent magnets at the sides of the substrate. The number of Pd chips and the rf power ratio between the two plasmas controlled the film composition, and sample thickness was determined by deposition time. Specimens were annealed at 473–613 K for 5 min in vacuum in an in-plane uniaxial field of 80 kA/m directed along the easy axis of the films.

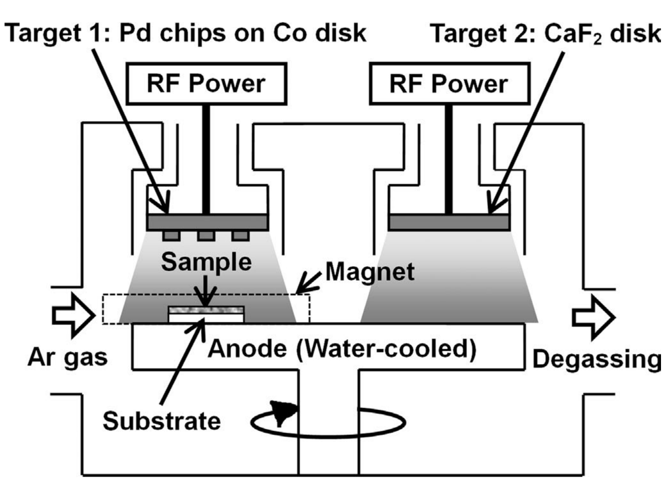

Fig. 1. Schematic of a tandem-sputtering deposition system.

Film composition was analyzed by energy disperse X-ray spectrometry (EDS) and wavelength dispersive X-ray spectrometry (WDS). The powder X-ray diffraction (XRD) patterns were measured using Cu-$K\alpha$ radiation to identify the crystallinity of the metallic granules and the fluoride matrix, and the phase separation. Their mean diameter were estimated using Scherrer equation [22]. The sample thickness was measured by a stylus surface profiler for measurement of the electromagnetic properties and deposition rate. Vibration sample magnetometer (VSM) was used to measure magnetization curves and the electrical dc resistivity was measured by the four-point probe method. The complex permeability spectra were measured by the shielded loop coil method [23] together with the all shielded-shorted microstrip line method [24] for the frequency range from 50 MHz to 14 GHz. Subsequently, they were numerically analyzed based on the Landau–Lifshitz–Gilbert (LLG) equation [25,26], where the saturation magnetization, anisotropy field, electrical dc resistivity, thickness, and Gilbert damping factor were applied. The cross-sectional nanostructures of specimens were observed in transmission electron microscopy (TEM) or scanning transmission electron microscopy (STEM) operating at 200 kV. Observation samples were prepared with a precision ion polishing system (PIPS). The magnetic domain structure was observed by MOKE domain observation equipment (Kerr microscope) with magnetic fields up to 80 kA/m. TMR was measured in a dc magnetic field ranging from 0 to ± 800 kA/m by the four-point probe method with a Helmholtz coil electromagnet. All data were taken at room temperature.

3. Results and discussion

3.1. Electrical resistivity

Fig. 2 presents a typical composition range of a CoPd–CaF_2 nanogranular system. In this study, the authors focused on a $(Co_{0.69}Pd_{0.31})_x$–$(Ca_{0.31}F_{0.69})_{100-x}$ (atomic percent) system. The chemical compositions of specimen analyzed by EDS are plotted in the figure. The solid line in the figure denotes the stoichiometric composition. The plots almost fit this line. The electrical dc resistivity ρ was plotted against chemical composition x as granule concentration (atomic percent) in Fig. 3 with previous results for oxide-based $(Co_{0.70}Fe_{0.30})_x$–$(a\text{-}AlO)_{100-x}$ [27] and $(Fe)_x$–$(a\text{-}MgO)_{100-x}$ [28] nanogranular systems included for comparison. Lines between plots are a guide.

ρ decreases monotonically as the chemical composition x increases. However, the ρ of CaF_2-based nanogranular films differs from that of amorphous AlO or MgO-based films. The differences in ρ increase with decreasing metallic granules (increasing matrix) and are independent of a kind of the metallic granules. We thus readily believed that the high resistivities of CaF_2-based