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High magnetization Co-GdO_x superparamagnetic granular films as magnetic coating materials for high-sensitivity alternating magnetic force microscopy tip

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ABSTRACT

The $Co_y(GdO_x)_{1-y}$, Co_yAg_{1-y}, $(Fe_{70}Co_{30})_y(AlO_x)_{1-y}$ superparamagnetic (SP) granular films were fabricated by magnetron co-sputtering technique and compared for their magnetic properties. The effect of the different matrix (GdO_x, Ag, AlO_x) is investigated for refining and separating magnetic particles in non-magnetic matrix by calculating the magnetic volume fraction (y), and the results indicate that the GdO_x matrix can more effectively refine and separate magnetic particles. The $Co_{0.44}(GdO_x)_{0.56}$ SP film with the maximum Co volume fraction (y = 0.44) approaches the highest magnetization of 608 emu/cm^3 at 20 kOe, and initial susceptibility (1.74×10^{-5} H/m) as compared with Co-Ag, $Fe_{70}Co_{30}$-AlO_x films and some systems of other researchers at room temperature (RT). The magnetic particle size and size distribution in these SP films is calculated by fitting with Langevin function and the results of calculation are consistent with the high-resolution transmission electron microscopy (HRTEM) results. To further confirm the SP behavior, the blocking temperature of the $Co_{0.44}(GdO_x)_{0.56}$ film with the maximum Co volume fraction is measured as ~145 K, which is below RT. Finally, the $Co_{0.33}(GdO_x)_{0.67}$ thin film having a linear magnetization curve is used for the fabrication of the SP tip and further used for the A-MFM measurement on the bulk Sr-Ferrite (SrF) magnet. The fabricated $Co_{0.33}(GdO_x)_{0.67}$ SP tip along with A-MFM shows an excellent result as compared to the state of art FePt hard magnetic tip using conventional MFM, and it can directly detect the intensity and identify the polarity of the stray field originating from a bulk Sr-Ferrite (SrF) permanent magnet without topography crosstalk in ambient atmosphere.

1. Introduction

Granular superparamagnetic (SP) films consist of nano-sized magnetic particles embedded in a non-magnetic matrix [1–3]. The persistent interest in this class of composite material is primarily due to their giant magnetoresistance or tunneling magnetoresistance (GMR or TMR), SP properties, high sensitivity sensors, and bio-applications [4–8]. The magnetic properties of granular films are determined by the intrinsic properties of magnetic particles and matrix [9], and the volume fraction of magnetic particles [10], the magnetic particle size, as well as size distribution. The main features of the magnetic behavior of these films are the presence of a SP-ferromagnetic (FM) transition by continuing to increase the magnetic volume fraction.

The SP thin film materials with the lack of hysteresis are attractive candidates for the fabrication of magnetic force microscopy (MFM) tips [11] and magnetic field sensors applications [12]. For the MFM tip application, the SP materials with high magnetization are highly desirable in order to enhance the sensitivity and to avoid the tip memory effect in MFM image introduced by the tip hysteresis of the conventional MFM tip. Also, the high magnetization SP films can increase the spatial resolution of MFM imaging by reducing the coating thickness for the SP tip. However, the fabrication of the SP material thin films with a high magnetization still remains an open challenge. In order to approach this aim, the SP granular films should have a structure with matrices (metal or oxide matrix) which can effectively refine and homogeneously separate the magnetic particles and prevent the exchange interactions between adjacent magnetic particles to get a very large critical magnetic volume fraction of SP-FM transition. Here, the selection of the matrix material is very important for getting the high magnetization SP film.

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Until now, the Co_yAg_{1-y} [13], Fe_yAg_{1-y} [14], Co_yCu_{1-y} [5,15], Fe_yCu_{1-y} [16], $Fe_y(SiO_x)_{1-y}$ [17,18], $Co_y(SiO_x)_{1-y}$ [19], $(Co_{50}Fe_{50})_y(AlO_x)_{1-y}$ [20] etc. granular films with SP properties had already been reported. In this work, we choose the GdO_x as a matrix by considering two main reasons. First, most important reason is the Gibbs free energy for the formation of Gd_2O_3 is −1730 kJ/mol which is higher than Al_2O_3 (−1582.31 kJ/mol) and SiO_2 (−856.4 kJ/mol) at room temperature (RT) [21]. It indicates that Gd atoms can easily form a stable GdO_x matrix by reacting with oxygen as compare to Al and Si atoms, and the GdO_x matrix can effectively refine and homogeneously separate the magnetic particles. Second, the paramagnetic susceptibility of Gd_2O_3 ($+53200 \times 10^{-6}$ cm^3/mol) matrix is higher as compared to the diamagnetic Ag (-19.5×10^{-6} cm^3/mol), Al_2O_3 (-37×10^{-6} cm^3/mol), Cu (-5.46×10^{-6} cm^3/mol) and SiO_2 (-29.6×10^{-6} cm^3/mol) matrices at RT [22]. Also, the RT magnetization of the GdO_x matrix is ~30 emu/cm^3 at 20 kOe. Considering the above said unique properties of the GdO_x matrix it is possible to prepare the SP film with a high magnetization by making the phase separated solid solution of GdO_x and Co.

In the present study, the effect of different matrices (GdO_x, Ag, AlO_x) is investigated for refining/separating the magnetic (Co, $Fe_{70}Co_{30}$) nanoparticles in non-magnetic matrix by calculating the magnetic volume fraction (y), in order to get the high magnetization granular SP films. It is demonstrated that the GdO_x matrix can more effectively refine and separate Co nanoparticle results in the $Co_{0.44}(GdO_x)_{0.56}$ film with highest Co volume fraction as well as magnetization respectively. For the proof of concept, the alternating magnetic force microscopy (A-MFM) tip is fabricated by using 100 nm $Co_{0.33}(GdO_x)_{0.67}$ SP film with linear magnetization curve and used for the magnetic domain imaging of the polished permanent Sr ferrite (SrF) magnet. The fabricated $Co_{0.33}(GdO_x)_{0.67}$ SP tip shows an excellent result as compared to the state of art FePt hard magnetic tip.

2. Experimental

The 100 nm thick Co_yAg_{1-y}, $(Fe_{70}Co_{30})_y(AlO_x)_{1-y}$ and $Co_y(GdO_x)_{1-y}$ films on thermally oxidized Si (001) substrates are prepared by magnetron co-sputtering technique by using individual magnetic elemental Co, $Fe_{70}Co_{30}$ targets with DC power and Ag, Al_2O_3, Gd_2O_3 targets for matrix element with RF power (100 W) under 10 mTorr Ar gas pressure. Before sputtering, the base pressure of the sputtering chamber was kept at 3×10^{-6} Torr, and during sputtering the substrates are rotated at 20 rpm to obtain a uniform granular state. The volume fraction of Co, $Fe_{70}Co_{30}$ in the matrix is controlled by changing the DC power (55–80 W, 20–40 W, 85–140 W) of sputtering magnetic elemental targets for Co_yAg_{1-y}, $(Fe_{70}Co_{30})_y(AlO_x)_{1-y}$ and $Co_y(GdO_x)_{1-y}$ respectively while keeping the other deposition parameters constant. The deposition rate of Ag, Al_2O_3 and Gd_2O_3 targets with RF power 100 W is 0.15 nm/s, 0.06 nm/s, and 0.18 nm/s, respectively.

The magnetic properties of all the films are measured by vibrating sample magnetometer (VSM, Toei Industry Co., Ltd., VSM-5S) with the maximum applied field 20 kOe. For the *M-T* curve measurement, the temperature range of VSM is from 94 K to RT. The microstructure of the deposited films is estimated by high-resolution transmission electron microscope (HR-TEM, JEOL, JEM-2100F). The morphology of the prepared SP tips is observed by scanning electron microscope (SEM, JEOL, JSM-6701F).

The SP tips are also fabricated by coating the 100 nm $Co_{0.33}(GdO_x)_{0.67}$ SP film on commercial pyramidal Si tip by using the same parameters as used before for the fabrication of thin films. The prepared SP tip is then used for the magnetic domain imaging of the polished Sr ferrite (SrF) permanent magnet. The A-MFM used the double-scan tapping-lift model in ambient atmosphere. The topographic signal is acquired by the first raster scan, and the magnetic signal is obtained by successive raster scans with a small lift height from the surface. In A-MFM measurement, an external AC magnetic field with frequency (ω_m) is applied to the SP tip. The magnetic moment of a SP tip is modulated by the external AC magnetic field. The interactive force between the modulated magnetic moment of the SP tip and the stray field of sample causes frequency modulation of the cantilever oscillation and produce a pair of side bands signals ($\omega_0 \pm \omega_m$) near the cantilever resonant frequency (ω_0). The modulation signals are frequency demodulated by using a phase-locked-loop (PLL) and are detected by the lock-in amplifiers. Here, the frequency and intensity of the applied external AC magnetic field is 89 Hz and 200 Oe_{o-p} (zero-to-peak), respectively. The scanning rate is 0.2 Hz, and the lift height is kept at 200 nm. The details of the A-MFM measurement set up can be found in the previously reported studies [23,24].

3. Results and discussion

Fig. 1(a) and (b) shows the in-plane *M-H* curves of the $Co_y(GdO_x)_{1-y}$ series films as function of Co volume fraction y at RT with the applied magnetic field 20 kOe and 100 Oe, respectively. Magnetization measurements demonstrated that no visible hysteresis is found for the films up to concentration of $y \leq 0.44$. The magnetic phase in the films of these compositions can be considered as an ensemble of small non interactive magnetic particles in SP state at RT. With increasing y, a gradual transition from SP to FM state occurs, as clearly shown in Fig. 1(b). In Fig. 1(b), for y = 0.46, the shape of the hysteresis loop shows contributions of FM and SP phases with coercivity (H_c) of ~7 Oe. Fig. 1(c)–(f) shows the calculation method for the magnetic volume fraction, and the magnetic particle radius for samples with y = 0.27, 0.44, respectively. The magnetic volume fraction (y) and the saturation magnetization (M_{SP}) of thin films are evaluated by Langevin function in the following way [25].

$$M(H) = M_{SP}\left[\coth\left(\frac{mH}{kT}\right) - \frac{kT}{mH}\right] \quad (1)$$

The saturation magnetization (M_{SP}) of the SP film can be given by using the magnetic volume fraction (y) and saturation magnetization (M_s) of magnetic phase multiplied, as follows:

$$M_{sp} = yM_s \quad (2)$$

Here by assuming the shape of magnetic particle as sphere with radius *r*, the magnetization of one particle (*m*), can be given by:

$$m = M_s \cdot \frac{4}{3}\pi r^3 \quad (3)$$

Here, the M_s is the saturation magnetization of Co (1440 emu/cm^3) and $Fe_{70}Co_{30}$ (1960 emu/cm^3), respectively [26].

When the magnetization approaches to the saturation in a high magnetic field, the Eq. (1) can be written as follows:

$$M(H) \cong M_{SP}\left[1 - \frac{kT}{mH}\right] \cong M_{SP} - \frac{M_{SP}kT}{mH} \quad (4)$$

By substituting Eqs. (2) and (3) in Eq. (4), Eq. (4) can be written as follows:

$$M(H) \cong yM_S\left[1 - \frac{kT}{mH}\right] = yM_S - \frac{yM_SkT}{mH} = yM_S - \frac{3ykT}{4\pi r^3 H} \quad (5)$$

Thus, when $H \to +\infty$, by calculating the intercept of *M*-1/*H* curve, the saturation magnetization M_{SP} of SP film and magnetic volume fraction y value can be evaluated. Concurrently, by