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Synthesis and magnetic properties of the thin film exchange spring system of MnBi/FeCo

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Abstract. Manganese bismuth thin films with a nominal thickness of ∼ 40 nm were grown at room temperature onto quartz glass substrate in a DC magnetron sputtering unit. In contrast to the usual multilayer approach, the MnBi films were deposited using a single sputtering target with a stoichiometry of $Mn_{55}Bi_{45}$ (at. %). A subsequent in-situ annealing step was performed in vacuum in order to form the ferromagnetic LTP of MnBi. X-ray diffraction confirmed the formation of a textured LTP MnBi hard phase after annealing at 330 °C. This film shows a maximum saturation magnetization of 530 emu/cm^3 and high out-of-plane coercivity of 15 kOe induced by unreacted bismuth. The exchange coupling effect was investigated by deposition of a second layer of FeCo with 1 nm and 2 nm thickness onto the LTP MnBi films. The MnBi/FeCo double layer showed as expected higher saturation magnetization with increasing thickness of the FeCo layer while the coercive field remained constant. The fabrication of the MnBi/FeCo double layer for an exchange spring magnet was facilitated by deposition from a single stoichiometric target.

1. Introduction

Synthesis of rare earth free permanent magnet materials has drawn much attention recently since the unreliable global market for rare earth elements made their application critical [1, 2]. Rare earth free magnets must have high magnetic anisotropy, high temperature stability, and high energy products to be considered as promising substitutes for rare-earth containing magnets [3]. Despite its relatively low theoretical saturation magnetization of 710 emu/cm^3 compared to the rare earth magnets, MnBi potentially has the required magnetic properties to be qualified as suitable candidate [4, 5, 6]. Particularly, it shows a positive temperature coefficient for coercivity and magnetic anisotropy which makes it even more interesting for high temperature applications [7, 8, 9]. It is possible to improve the magnetic moment and also the energy density for MnBi using it as hard magnetic component in combination with a soft magnetic phase in an exchange spring magnet configuration [10].

Although synthesis of MnBi thin films has been studied for long, the exchange coupling with a soft magnetic phase as a mean to improve its performance has been barely investigated so far. In contrast to the previous approach with multiple depositions of separate Bi and Mn layers used for preparation of MnBi thin films followed by a post annealing step [11, 12, 13, 14, 15, 16, 17], in this work we have established a novel more straightforward synthesis route. We have deposited MnBi thin films via a single step deposition from a $Mn_{55}Bi_{45}$ (at. %) stoichiometric sputtering target which provides us an easier way to deposit additional layers for spring magnet hetero-structure configurations.

2. Material and methods

Manganese bismuth thin films with a typical thickness of 40 nm were deposited on quartz glass substrates in a DC magnetron sputtering unit with a base pressure of $\sim 4.0\times10^{-6}$ Pa. We have used single stoichiometric sputtering targets with composition of $Mn_{55}Bi_{45}$ (at.%) and $Fe_{65}Co_{35}$ (at.%) for our depositions. The optimized growth rate was 0.04 nm/s for MnBi layer, and 0.008 nm/s for FeCo layer. The MnBi thin films were deposited at room temperature and subsequently annealed for 1 hr *in situ* under vacuum ($\sim 1.0\times10^{-5}$ Pa) at different annealing temperature. For the double layer system, the FeCo layer was deposited at room temperature on top of LTP MnBi annealed at 330 °C. The films were capped with a 10 nm thick tantalum layer to prevent oxidation. We have determined the phase composition by X-ray diffraction, the film thickness by a Bruker Dektak-XT surface profilometer, and the magnetic properties were measured using a SQUID magnetometer.

3. Results and discussion

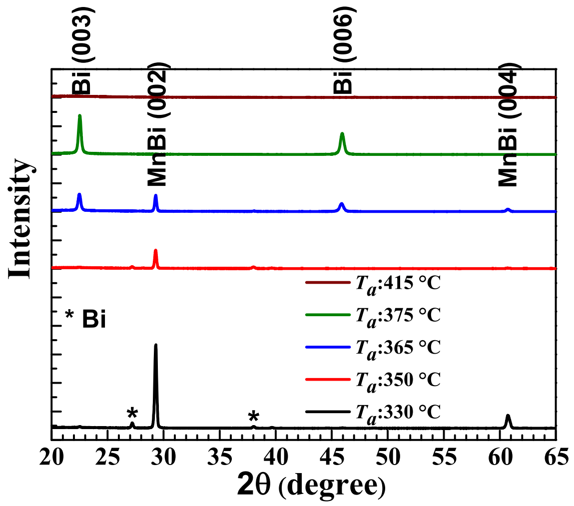

Figure 1. X-ray Diffraction patterns for MnBi thin films annealed at different temperatures, T_a, between 330 °C and 415 °C. For the purpose of clarity the spectra are vertically offset.

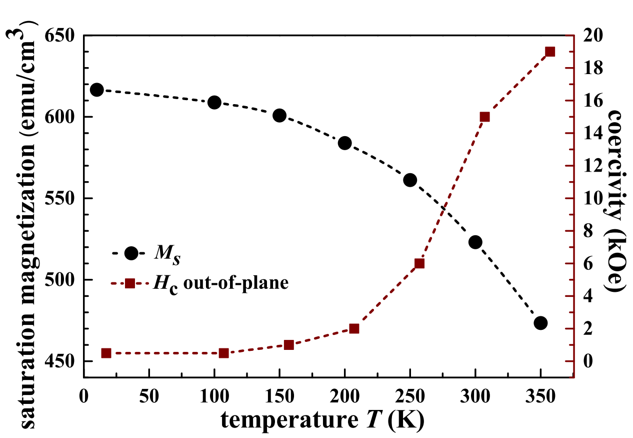

Figure 2. Saturation magnetization and out-of-plane coercivity as a function of temperature for a MnBi single layer (40 nm) annealed at T_a = 330 °C measured at different temperatures between 10 K to 350 K.

Fig. 1 contains room-temperature XRD patterns of MnBi thin films annealed at different temperatures in the range of 330 °C to 415 °C. The indexed peaks belong to hexagonal MnBi(with space group of $P63/mmc$) and also show traces of residual bismuth in the films. The MnBi (002) and (004) peaks appear with the highest intensity when T_a reaches 330 °C which indicates the formation of ferromagnetic LTP MnBi with c-axis texture. The Bi (003) and Bi (006) peaks were also observed but with much lower intensities. By increasing the annealing temperature, the intensity of MnBi ($00l$) peaks drops which is accompanied by an increase in the intensity of Bi ($00l$) reflections. This shows that the LTP MnBi starts to decompose into crystalline Bi and amorphous Mn. This trend continues until T_a above 415 °C at which the LTP MnBi phase is completely decomposed and no more reflections are visible. In comparison to a previous similar study, we have observed that the optimized temperature depends on the vacuum level where the annealing takes place: a better vacuum is associated with a lower optimal annealing temperature.

Fig. 2 shows the changes in volume saturation magnetization and out-of-plane coercivity at different temperatures between 10 K and 350 K for a MnBi thin film annealed at 330 °C. As it can bee seen, the saturation magnetization (M_s) decreases with increasing temperature from 610 emu/cm^3 at 10 K down to 470 emu/cm^3 at 350 K. On the other hand, the out-of-plane coercivity (H_c) is nearly zero below 150 K and grows drastically with further increase in temperature, as it is expected for LTP MnBi, and reaches 19 kOe at 350 K. The room-temperature M_s and H_c for the MnBi thin film annealed at 330 °C were 530 emu/cm^3 and 15 kOe, respectively. According to the XRD patterns in Fig. 1, some unreacted Bi is still present in this sample acting as an hindrance for domain wall motion leading to a high coercivity and a high energy density $(BH)_{max}=$ 8.7 MGOe for this sample.

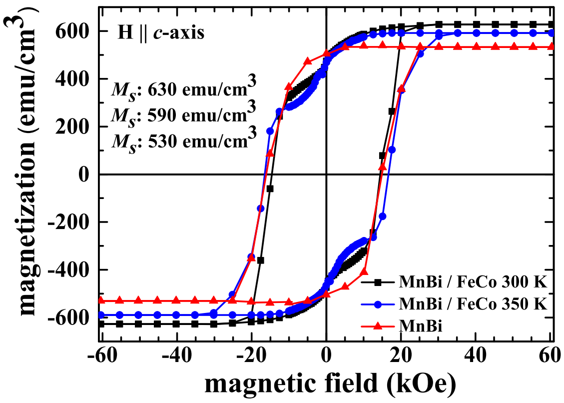

Figure 3. Out-of-plane magnetization data for a MnBi single layer (40 nm) measured at 300 K (red) and a MnBi(40 nm)/FeCo(1 nm) double layer measured at 300 K (black) and at 350 K (blue).

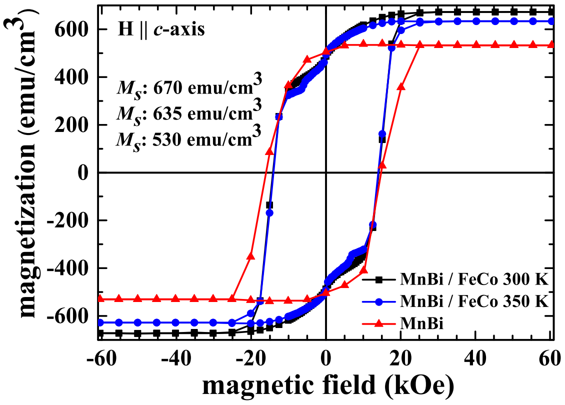

Figure 4. Out-of-plane magnetization data for a MnBi single layer (40 nm) measured at 300 K (red) and a MnBi(40 nm)/FeCo(2 nm) double layer measured at 300 K (black) and at 350 K (blue).

Fig. 3 and Fig. 4 show the hysteresis loops for the double layer of MnBi plus FeCo measured at 300 K and 350 K with 1 nm and 2 nm of FeCo as soft layer, respectively. In order to be able to compare these results, the magnetization data for the single MnBi film annealed at 330 °C is also included. We have grown the second layer of FeCo on top of MnBi at room-temperature with two different thicknesses. By addition of 1 nm and 2 nm of FeCo the saturation magnetization has increased as expected from 530 emu/cm^3 to 630 emu/cm^3 and 670 emu/cm^3, respectively. The coercivity, on the other hand, stays nearly constant. Comparing the graphs in Fig. 3 and Fig. 4 with the summarized graph in Fig. 2 for single MnBi layer at 300 K shows that the thermal stability has improved for the coupled layers. The kink in the hysteresis curve of the double layer indicates that the exchange coupling is incomplete, which is most likely due to the roughness of the interface. The interface roughness can be reduced by growing much thinner MnBi layers ($<$ 10 nm) at decreased deposition rates. The thickness of the hard magnetic layer in an exchange spring system anyhow should be as thin as possible, since this results in the largest increase of total magnetization.

4. Conclusions

LTP MnBi thin films with c-axis texture, high coercivity of 15 kOe and a maximum room-temperature energy product of $\sim$ 8.7 MGOe were deposited directly from a single stoichiometric $\mathrm{Mn}_{55}\mathrm{Bi}_{45}$ (at. %) sputtering target onto quartz glass substrates and subsequently annealed at $\sim$ 330 °C. In order to investigate the exchange coupling effect we have deposited a soft magnetic layer of FeCo on top of the MnBi thin film. The magnetization of the total system increased as expected while the coercivity remains unchanged. Since smooth interfaces are required to obtain an effective exchange path, our deposition approach working with a single MnBi layer with the targeted stoichiometry seems to be a promising way to enable the desired exchange coupling.

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