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Correlation between phase composition and exchange bias in CoFe/MnN and MnN/CoFe polycrystalline films

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ABSTRACT
Magnetic properties and phase composition of both MnN/CoFe (MnN at top of bilayer) and CoFe/MnN films (MnN at bottom of bilayer) bilayers through annealing at various temperatures (T_a = 300-450 °C) and then cooling to room temperature under the application of an external magnetic field of 1.5 kOe are compared. The exchange bias field (H_E), the magnitude of magnetic hysteresis loop shift, of the studied films is highly related to phase composition of antiferromagnetic (AF) layer. The increase of H_E with increasing T_a in the range of 300-375 °C possibly results from the improvement of magnetocrystalline anisotropy of AF related to the promoted crystallinity and stress relaxation of tetragonal face-centered θ-MnN phase. The reduction of H_E at higher T_a is due to the decreased volume fraction or disappearance of θ-MnN phase and the formation of impurity phases, such as Mn_4N and Mn. The induction of impurity phases is possibly related to the diffusion of part of N out of MnN phase at higher T_a. Higher H_E for CoFe/MnN than MnN/CoFe at T_a = 300-375 °C might be attributed to larger amount and higher degree of stress relaxation for θ-MnN phase. For CoFe/MnN film annealed at 375 °C, the highest H_E = 562 Oe is attained, and the corresponding interfacial exchange energy of 0.47 mJ/m^2 in this study is comparable to that reported by Meinert et al. [Phys. Rev. B 92, 144408 (2015)].

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I. INTRODUCTION
Nowadays spin electronics is becoming a significant technology and the foundation of spin-valve based devices, like giant magnetoresistance (GMR) and tunnel magnetoresistance (TMR) and so on. The spin-valve based devices mainly consist of a free layer and a pinned layer. In general, as a pinned layer, strong exchange bias (EB) between a FM layer and antiferromagnetic (AF) layer is requisite. EB, characterized by a shift of magnetic hysteresis loop, results from the interaction between the FM and AF layers. For practical EB system, the main requirements for AF layer are large magnetocrystalline anisotropy constant (K_{AF}), high Néel temperature (T_N), good corrosion resistance, ease of manufacturing, environmental safety and low price. Recently, MnN reported could meet the above requirements. AF MnN crystallizes at θ phase with tetragonal face-centered NaCl structure at room temperature (RT). Its T_N is about 660 K where this magnetic transition accompanies with a phase transformation from tetragonal to cubic.

Magnetic properties of MnN-based exchange bias system have been studied by Meinert. For in-plane CoFe/MnN films, large EB field (H_E) of 1800 Oe was obtained for very thin CoFe layer
of 1.6 nm in thickness. On the other hand, for perpendicular MnN/CoFeB/MgO/Ta films, \( H_E \) of 3600 Oe could be attained for ultrathin thin CoFeB layer of 0.65 nm in thickness. As EB effect is mostly an interface phenomenon, EB field (\( H_E \)) is highly sensitive to interface roughness, morphology, crystallinity, thickness and grain size of both FM and AF.\(^{14-16}\) In this work, we compare magnetic properties and phase composition of both MnN/CoFe (MnN at top of bilayer) and CoFe/MnN (MnN at bottom of bilayer) films with various annealing temperatures (\( T_a \)) in the range of 300–450 °C under the application of an external magnetic field of 1.5 kOe.

II. EXPERIMENT

CoFe/MnN and MnN/CoFe films with 5-nm-thick CoFe layer and 40-nm-thick MnN layer were prepared on 10-nm-thick Ta underlayer buffered glass substrates (Corning 1737) at RT by magnetron sputtering at the external in-plane magnetic field of 350 Oe induced by the NdFeB sintered magnet. The base pressure of the system was better than \( 5 \times 10^{-7} \) torr. MnN films were prepared from elemental Mn target at the ratio of Ar to \( N_2 \) atmosphere of 1:1. Subsequently, 3-nm-thick Ta was sputtered onto each samples to avoid oxidation. The post-annealing was performed at base pressure better than \( 5 \times 10^{-6} \) torr and various \( T_a \) in the range of 300–450 °C for 15 minutes, and then cooling to RT at the applied magnetic field of 1.5 kOe to align spins to form AF ordering and thus form in-plane EB. The structural characterization was carried out by x-ray diffractometer (XRD) using Cu \( K_a \) radiation. Magnetic properties were measured by an alternating gradient magnetometer (AGM). The thickness and surface morphology of the sample were measured by atomic force microscopy (AFM).

III. RESULTS AND DISCUSSION

XRD patterns of MnN/CoFe (MnN at the top layer) and CoFe/MnN (MnN at the bottom layer) films annealed at different temperature (\( T_a \)) within the applied magnetic field of 1.5 kOe are shown in Fig. 1(a) and (b), respectively. \( \theta \)-MnN(002) phase is found in both as-deposited films, while no diffraction peak from CoFe and Ta layers is detected due to too thin thickness. Distinct phase composition for two series films with \( T_a \) is observed. In MnN/CoFe films, with increasing \( T_a \), MnN(002) diffraction peak is shifted to higher angle attributed to the stress relaxation. The estimated d-spacing of (002) is reduced from 2.14 Å for as-deposited film to 2.09 Å for the film annealed at 400 °C. The strengthened intensity and the narrowed full width at half maximum (FWHM) of MnN(002) peak with the increase of \( T_a \) reveals grain growth. Mn\(_3\)N and Mn phases appear to coexist with MnN phase at \( T_a \) in range of 350–400 °C. At higher \( T_a = 450 \) °C, Mn\(_3\)N phase prevails.

On the other hand, for CoFe/MnN films, the peak shift to higher angle, the strengthened intensity and the narrowed FWHM for MnN(002) texture with increasing \( T_a \) are similar to above MnN/CoFe series films. The d-spacing of (002) is reduced from 2.151 Å for as-deposited film to 2.089 Å for the film annealed at 400 °C. Unlike above MnN/CoFe, no impurity phase is signed at \( T_a \) in the range of 300–375 °C for CoFe/MnN films. Mn\(_3\)N and Mn phases coexist with MnN phase at \( T_a = 400 \) °C. At higher \( T_a = 450 \) °C, Mn phase prevails.

Figure 2 shows the in-plane M-H curves of MnN/CoFe and CoFe/MnN films annealed at various temperatures. For MnN/CoFe films (MnN at the top layer), the shift of the M-H hysteresis loop along the negative direction of the applied magnetic field observed, shown in Fig. 2(a)–(d), reveals an EB. As shown in the inset of Fig. 2(a), EB found for the as-deposited MnN/CoFe film results from the aligned AF moment in MnN layer induced by aligned magnetic moment in CoFe layer due to the deposition of MnN/CoFe at the external magnetic field. In contrast, the symmetric M-H hysteresis loops observed for the as-deposited CoFe/MnN film (MnN at the bottom layer), shown in Fig. 2(e), indicates no exchange bias because the AF moment may not be directly aligned by external magnetic field of 350 Oe. Through post-annealing at various \( T_a \) in the range of 300–400 °C for 15 min. and then cooling to RT at the applied magnetic field of 1.5 kOe, the shift of the M-H hysteresis loop observed, shown in Fig. 2(e)–(h), reveals an EB due to the aligned AF moment in MnN.

Magnetic properties of two series films are summarized and shown in Figure 3(a) and (b). As shown in Fig. 3(a), for MnN/CoFe films, with increasing \( T_a \), \( H_E \) is increased from 32 Oe at as-deposited state to 165 Oe at \( T_a = 400 \) °C, and EB disappears at higher \( T_a = 450 \) °C. On the other hand, for CoFe/MnN films, with increasing \( T_a \), \( H_E \) is increased from 0 Oe at as-deposited state to 562 Oe at \( T_a = 350 \) °C.
then decreased to 369 Oe at $T_a = 400 \, ^\circ C$, and finally EB disappears at higher $T_a = 450 \, ^\circ C$.

$H_E$ of the above series films is highly related to phase composition of AF layer. The increase of $H_E$ with $T_a$ possibly results from the improvement of magnetocrystalline anisotropy of AF related to the promoted crystallinity and stress relaxation of $\theta$-MnN phase with $T_a$. The reduction of $H_E$ with further increasing $T_a$ is due to the decreased volume fraction or disappearance of $\theta$-MnN phase and...
the formation of impurity phases, such as Mn$_4$N and Mn, as shown in Fig. 1. The induction of impurity phases is possibly related to the diffusion of part of N out of MnN phase at higher $T_a$. Higher $H_E$ for CoFe/MnN than MnN/CoFe at $T_a = 300-375$ °C might be attributed to larger amount and higher degree of stress relaxation for $\theta$-MnN phase.

As shown Fig. 3(b), $H_c$ increases with increasing $T_a$ for 2 series films. $H_c$ increases from 21 Oe at as-deposited state to 400 Oe at $T_a = 450$ °C for MnN/CoFe films, while $H_c$ arises from 201 Oe at as-deposited state to 640 Oe at $T_a = 450$ °C for CoFe/MnN films. The change of $H_c$ with $T_a$ for two series films is possibly related to roughness of the interface between CoFe and MnN layers: in addition to phase composition, the main difference between MnN/CoFe and CoFe/MnN films is considered to the roughness of the interface between MnN and CoFe.

In order to infer the roughness of the interface, AFM images of the top surface for as-deposited CoFe and MnN films on Ta underlayers are studied and shown in Fig. 4 (a) and (b), respectively. The surface roughness ($R$) of MnN ($R = 0.4$ nm) is larger than CoFe ($R = 0.2$ nm). Higher interfacial roughness in CoFe/MnN than MnN/CoFe results in higher coercivity for CoFe/MnN. Fig. 4(c)–(f) show AFM images of the studied films. Clearly, very flat surface with low $R$, and therefore, good EB is induced. $R$ is summarized in Fig. 4(g). With increasing $T_a$, $R$ of below 1 nm is observed
at \( T_a \) lower than 375 \(^\circ\)C, and therefore, large \( H_E \) is attained. However, higher \( T_a \) leads to the intermixing and the diffusion of part of N out of MnN phase, sharply increases \( R \), and therefore decreases \( H_E \) and increases \( H_c \). Accordingly, the interfacial morphology also contributes to affect magnetic properties of the presented CoFe/MnN system with \( T_a \) in addition to phase composition.

IV. CONCLUSIONS

Structure and magnetic properties of thin film stacks containing CoFe and MnN layer deposited in different sequence are reported. Two series films annealed at \( T_a \) below 400 \(^\circ\)C mainly consist of \( \theta \)-MnN(002) phase, and the stress relaxation and grain growth of MnN(002) with increasing \( T_a \) are found. Distinct phase composition is found for two series films annealed at higher \( T_a \). For MnN/CoFe films, additional Mn\(_4\)N and Mn phases appear at \( T_a \) in range of 350-400 \(^\circ\)C, and Mn\(_4\)N phase prevails at higher \( T_a \) = 450 \(^\circ\)C. On the other hand, for CoFe/MnN films, additional Mn\(_4\)N and Mn phases also appear at \( T_a \) = 400 \(^\circ\)C, but Mn phase prevails at higher \( T_a \) = 450 \(^\circ\)C. With annealing, the coercivity increase results from 3 facts: phase segregation, interfacial intermixing, and grain growth. Besides, when MnN is at the bottom, \( H_E \) is larger due to less phase segregation, while \( H_c \) is also larger due to larger intermixing roughness.

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