The impact of Hf layer thickness on the perpendicular magnetic anisotropy in Hf/CoFeB/MgO/Ta films

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ABSTRACT

The impact of Hf layer thickness on magnetic anisotropy is evaluated for Hf/CoFeB/MgO/Ta multilayer films commonly used in magnetic tunnel junctions (MTJs). An easy-axis magnetization transition from the in-plane to the out-of-plane direction is observed when the thickness of Hf is greater than ~1.5 nm in our structure. Moreover, a critical Hf layer thickness exists for strong perpendicular magnetic anisotropy on the CoFeB/MgO interface that maintains the properties required for use in MTJs. We also perform X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM), and X-ray diffraction (XRD) to study the effects of film composition, chemical states, and crystallization on the magnetic anisotropy in Hf/FeCoB/MgO/Ta multilayers with Hf layers of various thicknesses.

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1. Introduction

Magnetic tunnel junctions (MTJs) based on CoFeB/MgO with perpendicular magnetic anisotropy (PMA) have rapidly become one of the most reliable and high-performance candidate materials for use in spintronic devices because of their high tunneling magnetoresistance ratio, high speed, low damping constant, and low power consumption [1–6]. Although the origin of PMA in nonmagnet/ferromagnet/oxide (NM/FM/oxide) structures is currently not well understood, the authors of one report claim that PMA originates solely from the FM/oxide interface [7]. In NM/FM/oxide multilayers, PMA can be optimized by adjusting parameters such as the compositions of the NM, FM, and oxide layers; the layer thicknesses; the magnetic dead-layer thickness; and the annealing treatment [8–10]. PMA is also influenced by oxidation conditions. For example, Manchon et al. reported that the PMA is extremely sensitive to the oxidation of the FM/oxide interface in the Pt/Co/AIOx system [11]. Chen reported that the interface oxidation migration plays an important role in magnetic anisotropy evolution from in-plane magnetic anisotropy to PMA in Pt/Co/MgO/Pt films [12]. The CoFeB composition also plays an important role in determining the magnitude of PMA. Moreover, PMA was reported to be larger in Fe-rich CoFeB/MgO films than in Co-rich CoFeB/MgO films [13].

The seed and capping layers in the seed/CoFeB/MgO/capped structure strongly affect the magnetic anisotropy of the CoFeB layers [14]. Underlayers such as Ta, Mo, W, Pt, and Pd have different effects on the PMA [15–17]. Liu et al. demonstrated that replacement of the Ta buffer by Hf leads to an enhancement of PMA in the CoFeB/MgO by as much as 35% [18]. However, the effects of Hf underlayer thickness on PMA have rarely been reported. Conceivably, a critical Hf underlayer thickness may exist, below which the Hf underlayer is no longer sufficiently thick to sustain good PMA. Here, we address this possibility in Hf/CoFeB/MgO/Ta multilayers. We observed that increasing the thickness of the Hf underlayer led to a transition of the easy axis of magnetization from the in-plane to the out-of-plane direction. The effects of the composition, interfacial chemical states, and crystallization on the magnetic properties of Hf/CoFeB/MgO/Ta multilayers were studied as well.

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2. Experimental details

Samples with a Hf(t)/CoFeB(1.1 nm)/MgO(2 nm)/Ta(2 nm) structure were deposited onto thermally oxidized Si/SiO$_2$ substrates via magnetron sputtering at a base pressure of $3.0 \times 10^{-8}$ Torr and a sputtering pressure of 3 mTorr of 99.99% Ar gas, where $t$ is the Hf layer thickness of 0.5, 0.75, 1.0, 1.5, 2.5, 3.5, or 10 nm. The substrates were rotated at 40 rpm during deposition to ensure uniform film thickness. After deposition, the samples were annealed at 250 °C for 30 min in a vacuum furnace in the absence of an external magnetic field and under a pressure of $4 \times 10^{-7}$ Torr. The magnetic properties were measured using a vibrating sample magnetometer at room temperature. The elemental chemical states were investigated via X-ray photoelectron spectrometry (XPS, ESCALAB 250Xi). The samples were introduced into a MICROLAB MK II X-ray photoelectron spectrometer after being removed from the deposition system. The vacuum of the analysis chamber was better than $3 \times 10^{-8}$ Torr. The Al K$_\alpha$ line at 1486.6 eV was used, with the X-ray source operated at 14.5 kV. The energy analyzer was operated at a constant pass energy of 50 eV. First, the samples were sputtered using low-energy Ar$^+$ ions to remove the Ta protective layer and other layers. (The sputter rate of Ar$^+$ ions to Ta protective layer and other layers had been accurately calibrated.) The Ar$^+$-ion current density was 50 mA/cm$^2$. Simultaneously, XPS data were recorded at a 90° take-off angle for photoelectrons with respect to the samples’ surface plane. Then, Ar$^+$-ion etching XPS was used to study the films at different depths. All binding energies were corrected for the sample charging effect with reference to the C 1s line. The microstructures were characterized by high-resolution transmission electron microscopy (HRTEM) (Tecnai F20) and X-ray diffraction (XRD).

3. Results and discussion

Schematics of the in-plane and out-of-plane magnetic hysteresis (MH) loops of Hf(t)/CoFeB(1.1 nm)/MgO(2 nm)/Ta(2 nm) with different $t$ are shown in Fig. 1a–f. Whereas samples with $t_{\text{Hf}} = 0.5$, 0.75, or 1.0 nm exhibit in-plane magnetic anisotropy, the magnetic anisotropy becomes out-of-plane when the Hf layer thickness in our multilayer structure exceeds ~1.5 nm. In the case of $t_{\text{Hf}} = 3.5$ or 10 nm, the out-of-plane magnetic hysteresis loops with high remanence and good squareness demonstrate that the easy axis of magnetization is perpendicular to the films’ plane. In the W buffer case, the PMA properties for W/CoFeB/MgO/Ta were clearly observed when the W thickness ranged from 1.8 to 7.4 nm [19]. The results also show that a minimum Ta thickness is required to maintain a strong perpendicular easy axis in Ru/Ta/CoFeB/MgO films [20].

Fig. 2a shows the dependence of the effective magnetic anisotropy on the Hf layer thickness for Hf(t)/CoFeB/MgO/Ta multilayer films. The effective magnetic anisotropy energy ($K_{\text{eff}}$) is determined for each sample using the following expression [21–23]:

$$K_{\text{eff}} = H_k \times M_s / 2,$$

where $M_s$ is the saturation magnetization and $H_k$ is the effective PMA field along the hard axis. A negative $K_{\text{eff}}$ is known to imply in-plane anisotropy. Here, we observed that the $K_{\text{eff}}$ is negative below the thickness of $Hf = 1.5$ nm. For thicker films, the Hf layer thickness in the structure is greater than 1.5 nm; the $K_{\text{eff}}$ values become positive in a certain range of Hf layer thicknesses in this study, indicating that the magnetic anisotropy becomes perpendicular to the film plane. $K_{\text{eff}}$ increases rapidly with Hf layer thickness and then reaches a maximum value of 3.49 Merg/cm$^2$ at $t_{\text{Hf}} = 2.5$ nm, beyond which the $K_{\text{eff}}$ values begin to decrease to 1.64 Merg/cm$^2$ at $t_{\text{Hf}} = 10$ nm. Fig. 2b shows the Ms dependence on the Hf layer thickness for Hf(t)/CoFeB/MgO/Ta multilayer films. The $M_s$ increases from 1450 to 2250 emu/cm$^3$ at $t_{\text{Hf}} = 1.0$ nm, slightly decreased to 1310 emu/cm$^3$ at $t_{\text{Hf}} = 3.5$ nm, and then dramatically decreased to 770 emu/cm$^3$ at $t_{\text{Hf}} = 10.0$ nm.

To clarify the effects of Hf underlayer thicknesses on PMA, we investigated the properties of the MgO layer as a barrier and the interface of CoFeB/MgO using XPS, HRTEM, and XRD analysis techniques.

XPS is one of the most widely used tools for investigating the chemical bonding and oxidation states of materials. We carefully performed an etching process for the multilayer thin-film samples using a time step varying between 0 and 75 s. On the basis of the XPS spectra of Ta, Mg, Co, Fe, and Hf, we characterized the CoFeB/MgO interface during the Ar$^+$-ion etching process. Fig. 3a–f shows the Fe 3p, O 1s, Ta 4f, and Hf 4f XPS spectra. Fig. 3a and b shows high-resolution Fe 3p XPS spectra and the computer-fitted curves for the samples with $t_{\text{Hf}} = 0.75$ and 3.5 nm and subjected to etching for 15 s, which corresponds to the CoFeB/MgO interface. According to the XPS handbook [24], the peaks located at −52.5 (peak 1) and −54.4 (peak 2) correspond to the metallic Fe 3p and Fe oxide 3p states, respectively. These results indicate that the interfacial Fe atoms were partially oxidized. However, the ratio of Fe oxide to metallic Fe calculated from the area of the fitted curves is 0.28:1 for the sample with 0.75-nm Hf and 0.58:1 for the sample with 3.5-nm Hf. These results indicate that the Fe in the film with $t_{\text{Hf}} = 3.5$ nm was more oxidized than the Fe in the film with $t_{\text{Hf}} = 0.75$ nm. Because of the origin of PMA in CoFeB/MgO structures is the hybridization of Fe (Co) and O orbitals at the interface of CoFeB/MgO, we observed strong PMA for the $t_{\text{Hf}} = 3.5$ nm sample because the Fe oxide layer formed in $t_{\text{Hf}} = 3.5$ nm is thicker than that formed in the $t_{\text{Hf}} = 0.75$ nm sample.

Fig. 3c and d shows high-resolution XPS spectra of the O 1s region and the corresponding computer-fitted curves for samples with 0.75- and 3.5-nm Hf and subjected to etching for 15 s, respectively. The spectrum for the sample with $t_{\text{Hf}} = 0.75$ nm exhibits a slightly smaller peak at −532 eV (peak 2) and a dominant peak at −530 eV (peak 1), which is attributable to the O atom in the MgO layer. For the sample with $t_{\text{Hf}} = 3.5$ nm, XPS spectra display a weak peak at −532 eV (peak 2) and a strong O 1s peak at −530 eV (peak 1). On the basis of previous research, the clear presence of substantial amounts of BO$_x$ [25,26], we attribute the higher BE peak at −532 eV to BO$_x$, as discussed below. However, as calculated from the area of the fitted curves, the ratio of O atoms in the BO$_x$ to O atoms in the MgO is 0.61:1 in the sample with 0.75-nm-thick Hf and 0.18:1 in the sample with 3.5-nm-thick Hf. These results indicate that more BO$_x$ was formed at the CoFeB/MgO interface for the sample with 0.75 nm Hf. The clear appearance of BO$_x$ peaks indicates that B atoms diffused toward either the CoFeB/MgO interface or the MgO layer. The CoFeB/MgO heterostructures demonstrate strong interface PMA features that are attributed to the hybridization of Fe (Co) and O orbitals at the interface of CoFeB/MgO; in addition, as previously discussed, XPS measurements show that the Fe oxide peaks are very weak for $t_{\text{Hf}} = 0.75$ nm films. On the basis of the B-atom diffusion and the presence of the BO$_x$ peaks in the $t_{\text{Hf}} = 0.75$ nm films, we attribute the very weak Fe oxide peak in the spectra of the $t_{\text{Hf}} = 0.75$ nm films to the consumption of the O liberated by the reduction of Fe oxides by the diffusing B atoms. This interpretation indicates that Fe oxide was reduced through the formation of BO$_x$ [27].

First-principles calculations have demonstrated that the bonding between Fe 3d and O 2p orbitals can give rise to PMA. The oxidation conditions play an essential role in PMA. The largest PMA value is obtained for ideal interfaces, whereas it is reduced in cases...
of over- or underoxidized interfaces [28]. In our research, the aforementioned analysis shows that formation of effective Fe–O orbital hybridization at the CoFeB/MgO interface is the critical factor for generating PMA in Hf(t)/CoFeB(1.1 nm)/MgO(2 nm)/Ta(2 nm) films. The formation of B oxide and the simultaneous reduction of Fe oxide at the bottom interface suggest that B oxide formation negatively affects PMA of the interface under thermal annealing. The BOₓ formed in the sample with \( t_{\text{Hf}} = 0.75 \) nm implies

Fig. 1. The magnetic hysteresis curves under in-plane and perpendicular magnetic fields applied to the films with a Hf(t)/CoFeB(1.1 nm)/MgO(2 nm)/Ta(2 nm) multilayer structure with \( t_{\text{Hf}} = 0.5 \) (a), 0.75 (b), 1.5 (c), 2.5 (d), 3.5 (e), and 10 (f) nm.

Fig. 2. The dependence of \( K_{\text{eff}} \) on the Hf layer thickness (a); the dependence of \( M_s \) on the Hf layer thickness (b) in Hf(t)/CoFeB(1.1 nm)/MgO(2 nm)/Ta(2 nm) multilayer structure.
the reduction of Fe oxides (underoxidized interfaces), which is detrimental for PMA. The formation of a moderate Fe oxide at the CoFeB/MgO interface was found to be critical for the large enhancement of the PMA ratio for Hf/CoFeB/MgO/Ta films with $n_{\text{Hf}} = 3.5$ nm after thermal annealing.

Fig. 3e and f shows the Hf 4f and Ta 4f XPS spectra for samples with $n_{\text{Hf}} = 0.75$ nm and $n_{\text{Hf}} = 3.5$ nm and subjected to different etching times. The XPS spectra exhibit strong spin—orbit splitting with the metallic Hf, Hf oxide, metallic Ta, and Ta oxide peaks. XPS peak 1 at $-14.3$ eV and peak 2 at $-16.1$ eV are characteristic of the metallic Hf 4f/2 and 4f/5/2 peaks, respectively. Peak 3 at $-18.2$ eV and peak 4 at $-19.5$ eV correspond to the Hf oxide 4f/2 and 4f/5/2 peaks, respectively. Peak 5 at $-21.5$ eV and peak 6 at $-23.1$ eV are characteristic of the metallic Ta 4f/2 and Ta 4f/5/2 peaks, respectively. Peak 7 at $-26.2$ eV and peak 8 at $-28.1$ eV correspond to the Ta$_{15}$ 4f/2 and Ta$_{15}$ 4f/5/2 peaks in Ta$_2$O$_5$, respectively. The XPS results show that both Ta and Ta$_{5+}$ were present on the surface of the film. Ta$_2$O$_5$ was formed in the air when the sample was transferred from the deposition system to the XPS system. At an etching time of 0 s, Ta$_{5+}$ became dominant over Ta and the intensity of the Ta$_{5+}$ peak became much higher than that of Ta. An increase in the etching time resulted in a substantial enhancement of the Ta peak intensity and a weakening of the Ta$_{5+}$ peak. At an etching time of 30 s, only Ta was present in the films. The XPS results show that the Ta surface was most oxidized and that only Ta was present in the films, as shown in Fig. 3e and f. Inspection of Fig. 3e and f shows that Hf oxide was formed in the sample with $n_{\text{Hf}} = 0.75$ nm because of the oxidation of the Hf adjacent to the Si/SiO$_2$ substrate on the bottom of the sample by SiO$_2$. Fig. 3f shows that Hf atoms did not remain at the bottom of the film but rather migrated to the film surface. At an etching time of 0 s, only small Hf signals were distinguished and the two Hf peaks were weak, demonstrating that only metallic Hf was present in the film surface. The intensity of the Hf peak was enhanced with increasing etching time. Notably, at etching times of 15 and 30 s, the corresponding Hf 4f spectra display not only the peaks due to metallic Hf but also the peaks arising from the Hf oxide present in the films. When the etching time was increased to 45 s, the corresponding Hf 4f spectrum only showed oxide Hf components, with no detectable trace of metallic Hf peaks. The Hf oxide was formed in films by oxidation of Hf by the adjacent SiO$_2$.

We introduced the Ellingham diagram of Hf and Si to analyze the results of oxides of Hf. This analysis is usually used to evaluate...
the ease of reduction of metal oxides. The lower the position of the plots of a metal in the Ellingham diagram is, the greater is the stability of its oxide. A reduced substance (such as a metal) whose Gibbs free energy of formation is lower on the diagram at a given temperature will reduce an oxide whose free energy of formation is higher on the diagram [29]. The Ellingham curve for Hf lies below the curves for Si, which indicates that Hf can be used as the reducing agent for oxides of Si. As shown in Fig. 4, the reducing agent Hf, whose Gibbs free energy of formation is lowest in the diagram at a given temperature, will reduce the oxidized Si, whose free energies of formation are higher on the diagram.

Metal thin films vacuum deposited onto SiO$_2$ substrates made from thermally oxidized Si wafers may react with SiO$_2$ [30]. The change in Gibbs free energy for this reaction is negative (i.e., the reaction is thermodynamically favorable). In this study, the atoms sputtered from the target and onto the substrate were provided with a kinetic energy of approximately several to tens of electron volts. Therefore, the reaction is dynamically possible. When a Hf thin film was vacuum deposited onto an oxidized Si wafer, Hf oxide was formed at the Hf/SiO$_2$ interface. Determination of the origins and the mechanism of the Hf migration to the interface of the film requires further research and discussion.

The HRTEM image of Hf(10 nm)/CoFeB(1.1 nm)/MgO(2 nm)/Ta(2 nm) deposited onto a thermally oxidized Si substrate after the annealing at 250 °C is shown in Fig. 5a. The bottom region of the Hf layer (approximately 1 nm) adjacent to the Si/SiO$_2$ substrate exhibits an amorphous structure. The amorphous film may be HfO$_x$ because Hf can be oxidized by SiO$_2$ according to the XPS results. The remaining region in the Hf layer in the sample is well crystallized and is clearly textured along the (002) direction. The MgO layer is mostly crystallized. The interfaces between the layers are sharp and smooth. The HRTEM images reveal complete crystallization of the Hf layer into the (002) texture for the film with an Hf layer thickness of 10 nm. Whereas the Hf layer of the structure has a (002) texture, the CoFeB and MgO layers exhibit bcc (001) and fcc(001) textures, respectively. These results suggest that Hf is an effective material for achieving good crystallization of MgO and CoFeB layers upon annealing at 250 °C. This good match of the crystallization between Hf and CoFeB layers also affects the crystallization of MgO, which may explain the observation of higher interface magnetic anisotropy in Hf-based structures compared to Ta-based and W-based structures [17,31].

The XRD pattern for Hf(10 nm)/CoFeB(1.1 nm)/MgO(2 nm)/Ta(2 nm) annealed at 250 °C is shown in Fig. 5b. A strong diffraction peak is observed at 35.4°, which corresponds to the Hf (002) peak. This result is in agreement with the HRTEM results. A very weak peak located at 32.3° is also observed, which corresponds to Hf (100). Our results show that a minimum Hf layer thickness is required to set up a perpendicular easy axis in Hf/CoFeB/MgO/Ta multilayers. The minimal Hf layer thickness observed in this study was 1.5 nm. We reasonably conclude that as the Hf thickness approaches or exceeds this value, it will develop PMA.

4. Conclusion

We have demonstrated the seed-layer thickness dependence of the PMA in the Hf(t)/CoFeB/MgO structure. Whereas the thinner Hf layer (<1.5 nm) displayed in-plane magnetic anisotropy, a gradual enhancement in PMA was observed with increasing Hf layer thickness (>1.5 nm). Moreover, a minimum Hf layer thickness of 2.5 nm was required to maintain a strong perpendicular easy axis of magnetization. XPS analysis revealed that some incorporation of some B into the MgO may adversely affect the PMA if the B is oxidized to BO$_x$. The formation of moderate Fe oxide at the CoFeB/MgO interface was observed to be critical for enhancing the PMA ratio. HRTEM images demonstrated the crystallization of Hf(002), CoFeB(001), and MgO (001) textures and indicated that smooth and clear interfaces were observed in the 10-nm Hf seed layer.
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References