

High Electronegativity Element Compounds as Way of Increasing Ferromagnetic Interface PMA and its Voltage Control

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Abstract

In this research was investigated influence of fluorine on the PMA energy at CoFeB interface as well as its influence on voltage control of PMA. Two fluorides, AlF₃ and MgF₂ were examined as source materials, and PMA energy rise was observed for both. XPS measurements prove ferromagnetic-F bonds creation and its dominance at the CoFeB interface.

1. Introduction

MRAM, based on TMR in magnetic tunnel junctions (MTJ) with perpendicular magnetic anisotropy (PMA) at the ferromagnetic/dielectric interface takes attention in last decade, because of its good performance as non-volatile memory and higher integration density [1, 2]. Spin-transfer torques is common way of changing free ferromagnetic layer magnetization, but in MTJs with PMA control of magnetization could also be provided by applying voltage bias to ferromagnetic/oxide interface; it is easier and decreases energy consumption.

Resultant magnetic anisotropy of the ferromagnetic layer is determined by energies comparison in eq. (1) of in-plane shape anisotropy and out-of-plane interface PMA:

$$K_{eff} = -\frac{1}{2}\mu_0 M_S^2 + \frac{K_{int}}{t_{eff}}, \quad (1)$$

where K_{eff} is magnetic anisotropy per unit volume, μ_0 – magnetic permeability of vacuum; M_S – saturation magnetization, K_{int} – interface magnetic anisotropy energy; t_{eff} – effective thickness of ferromagnetic. The value of K_{int} could be controlled by voltage what is commonly explained by changes in relative electron occupancy of d orbitals of ferromagnetic at the ferromagnetic/oxide interface [3, 4]. We expected that K_{int} would increase if oxygen at the interface is changed to another element with higher electronegativity, but possibility of voltage control would be preserved. Fluorine was chosen as such since it has very high electronegativity. The main objective of this study is clarifying of fluorine introduction influence on PMA and its voltage control.

2. Sample Fabrication and Characterization

AlF₃ and MgF₂ were used as fluorine source. Several structures were prepared, depending on purposes, where AlF₃, MgF₂, Al₂O₃, HfO₂ were grown by RF-sputtering; Ta, CoFeB – by DC-sputtering, Au – by vacuum evaporation, using Si covered with thermally grown SiO₂ as a substrate.

To characterize magnetic properties of stacks we used polar magneto-optic Kerr effect (MOKE) measurement under out-of-plane magnetic field and superconducting quantum interference device magnetic property measurement system (SQUID MPMS). Samples were annealed at 250°C (for MgF₂ stacks) and 300°C (for AlF₃, Al₂O₃ stacks) in nitrogen atmosphere for 10 minutes. Some samples were characterized by X-ray photoelectron spectroscopy (XPS) with Mg-k_α X-ray source.

3. Results and Discussions

At first approach fluorine was added by AlF₃ layer. It was found that if layer is thicker than 1.2 nm CoFeB layer lose its

ferromagnetic properties. Despite this, samples with 0.5 nm-thick AlF₃ layer covered with Al₂O₃ cap layer show decreasing in saturation magnetic field, what indicates increasing of PMA. Hysteresis curve is very sharp with close to zero saturation field, i.e. perpendicular magnetization of CoFeB layer. This result indicates a positive influence of fluorine, even though suppression of the effects of oxygen, by reducing oxygen interdiffusion, or oxide/fluoride intermixing with ferromagnetic layer would be required to clarify the advantage more clearly.

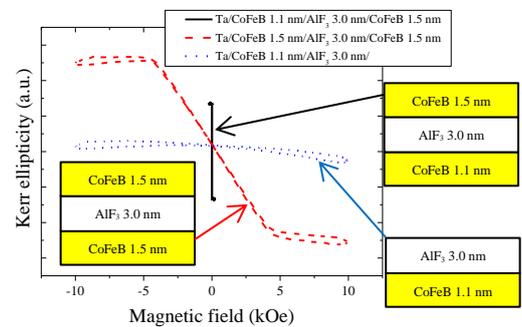


Fig. 1 MOKE measurements for stacks with 3.0 nm AlF₃ layer and 0, 1.5 nm CoFeB cap layers.

To exclude oxide from stack structures, the CoFeB cap layer was introduced to form the stacks: Si/SiO₂ 100 nm/Ta 4.0 nm/CoFeB 1.1, 1.5 nm/AlF₃ 3.0 nm/CoFeB 0, 1.0 or 1.5 nm. As shown in Fig. 1, the cap layer interface did not influence on magnetization anisotropy of the stack, since magnetization is out-of-plane for 1.1 nm bottom CoFeB layer and in-plane for 1.5 nm, even though the 1.5 nm-thick CoFeB cap layer should have in-plane anisotropy. But we found the cap layer also shown a minor contribution to anisotropy of the stack because when presumable magnetization directions of both cap and bottom layers matches overall measured magnetization increases, as shown in Fig. 2 (a) and (b).

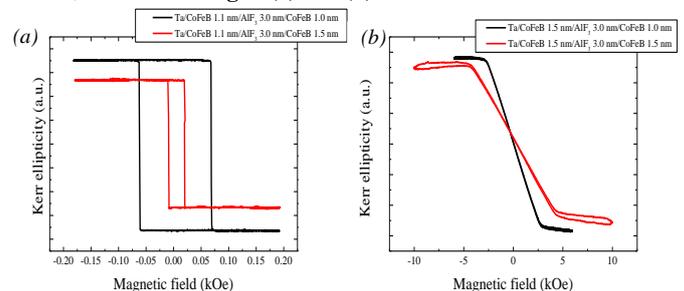


Fig.2 MOKE hysteresis loops for stacks with in-plane (1.5 nm) and out-of-plane (1.0 nm) magnetization of cap layers; (a) stacks with 1.1 nm bottom layer, (b) stacks with 1.5 nm bottom layer. Not capped stack didn't show ferromagnetic properties.

From eq. (1) it is clear that $K_{eff} \cdot t_{eff}$ should linearly correlates with t_{eff} , and intercept with $K_{eff} \cdot t_{eff}$ axis would gives K_{int} value. Fig. 3 shows that t_{eff} in the stacks with 0.5 nm-

thick AlF_3 layer increases in comparison to Al_2O_3 pure interface. Inset demonstrates the difference in saturation fields for structures with 1.1 nm-thick CoFeB stacks with or without fluoride layer. The stack with fluoride has almost zero saturation field and sharp magnetization reversal.

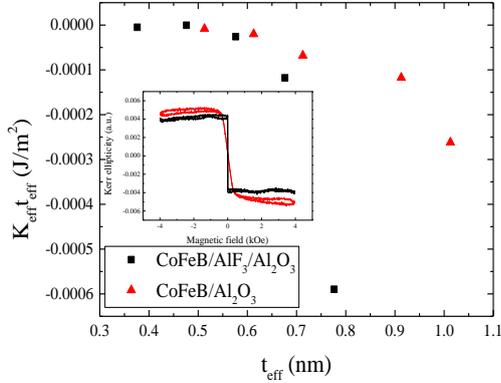


Fig. 3 Effective ferromagnetic thickness dependence of $K_{eff} \cdot t_{eff}$.

To prove possibility of voltage control of PMA stack: **Si/SiO₂ 100 nm/Ta 2.9 nm/CoFeB 1.1 nm/AlF₃ 0.5 nm/Al₂O₃ 4.0 nm/HfO₂ 30 nm/Au** was fabricated, and MOKE measurement was performed with applied voltage bias (**Fig. 4**). From this voltage dependence coefficient of PMA energy (K_{int}) to applied electric field, $\alpha \equiv |\Delta K_{int}/\Delta E| \approx 14 \text{ (fJ} \cdot \text{V}^{-1} \cdot \text{m}^{-1})$, was calculated, where E is defined as the applied effective electric field across the whole dielectric layer ($\text{Al}_2\text{O}_3 + \text{HfO}_2$). This value is not as large as the reported values in literature for CoFeB/MgO interfaces [4, 6], however it should be noted that it is larger in comparison to previously reported values for CoFeB/ Al_2O_3 stacks [5].

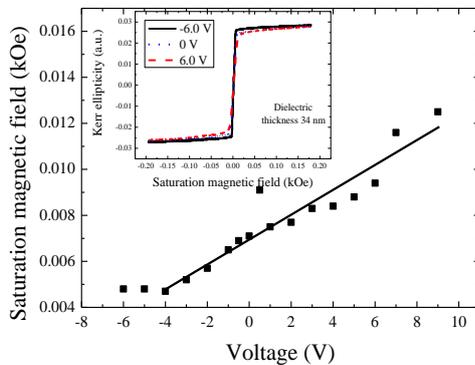


Fig. 4 Applied voltage dependence of saturation field. Inset shows hysteresis loops with ± 6 and 0 V voltage applied. Positive bias is corresponding to positive voltage appliance on top Au contact.

Taking account of the superior voltage control ability reported for CoFeB/MgO [6], MgF_2 is another candidate fluoride to be inserted for CoFeB/dielectric interface. It was observed that stacks with thick (3.0 nm) MgF_2 could provide higher PMA than structures with pure oxide interface and even without any capping layer (data not shown), what suggests the advantage of MgF_2 compared to AlF_3 from viewpoint of device structure fabrication.

To compare the efficiency of fluoride introduction in stacks with AlF_3 and MgF_2 layers the XPS measurements on **SiC/Ta 4.0 nm/CoFeB 1.1 nm/AlF₃ 3.0 nm/CoFeB 1.0 nm** and **Si/Ta 4.0 nm/CoFeB 1.2 nm/MgF₂ 3.0 nm** structures were performed. SiC or Si without any thermal oxide were employed as the substrate for this experiment to suppress the possible

contribution of SiO_2 to O1s core level spectra. From the comparison of signal intensities of F1s, Al2p and Mg2p core level XPS was found that AlF_3 layer have very low fluorine content in comparison to aluminum even if we take account of the amount of oxygen, included in this layer to substitute fluorine partially, thus Al-Al bonds could be presented at the interface, what could be the reason of lack of ferromagnetic properties in the stacks with thicker AlF_3 layer cases (as discussed in section 3.1). On the other hand MgF_2 show relatively close to stoichiometric F:Mg ratio even after annealing and prove itself as much more resistant to oxidation in the atmosphere (**Fig. 5**). Thus we can expect the selection of more suitable fluoride materials would be beneficial to enhance the fluorine introduction effects on the data shown in **Fig. 1 – 4**.

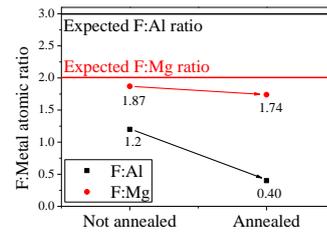


Fig. 5 Comparison of F to metal atomic ratios of stacks with aluminum and magnesium fluorides, using F1s, Al2p and Mg2p core level XPS data.

From the Co2p core level XPS (**Fig. 6 (a)**) the chemical bonds at the interface are inferred. We could attribute the sub-peak in Co2p to Co-F bonds formation, since the binding energy difference of those peaks agrees with the chemical shift of CoF_2 and CoF_3 in literature [7, 8]. In addition the angular-resolved XPS for structure **Si/SiO₂ 100 nm/Ta 4.0 nm/CoFeB 1.1 nm/MgF₂ 3.0 nm** (**Fig. 6 (b)**) showed monotonic decrease of F:Mg and F:O ratios to the surface, which indicates that more fluorine exists near interface, and oxygen remains near to the surface.

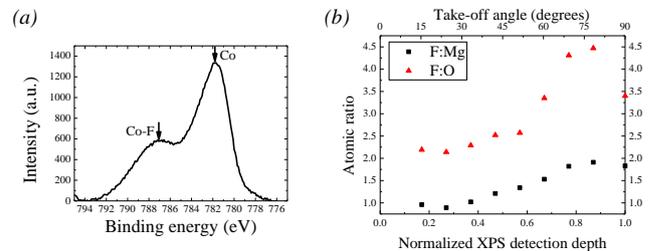


Fig. 6 XPS data of Co2p region of binding energies (**a**) and depth profile of atomic ratios in MgF_2 obtained by angular-resolved XPS (**b**). F:O ratio at 90° possibly comes from contamination of CoFeB target inside deposition chamber or it is signal from thick SiO_2 substrate.

4. Conclusions

In this study we found that the addition of fluorine as high electronegativity element to the interface increases PMA of CoFeB stacks in comparison to pure oxide interface. Not only PMA energy rise was observed, but also possibility of voltage control enhancement was suggested in the stacks with AlF_3 layer. MgF_2 will also fit for this purpose and XPS analysis showed dominance of Co-F bonds at the ferromagnetic interface

References

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