A comprehensive Study of Sign Change in Electric Field Control Perpendicular Magnetic Anisotropy Energy at Fe/MgO Interface: First Principles Calculation

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Electric field (EF) control on magnetic anisotropy energy (MAE) in the system which contains Fe/MgO interface with Cr underlayer was performed by means of first-principles electronic structure calculations. An opposite sign in EF coefficient (γ) was observed by introducing Fe/Cr intermixing. This intermixing leads to a substantial rearrangement in the electronic structure due to proximity effects of Fe and Cr. The origin of such an opposite sign in γ was discussed along the modulation of occupied and unoccupied d-band near the Fermi level. By introducing strain effect, the enhancements of MAE and γ were achieved with the maximum absolute values, 2.43 mJ/m^2 and 170 fJ/Vm respectively. The present result provides a new possible degree of freedom for the EF control in MAE as the underlayer configuration.

***Index Terms*—Magnetic anisotropy energy, proximity effect, strain effect, voltage control magnetic anisotropy energy.**

I. Introduction

A new perspective in utilizing electric field (EF) control of magnetic anisotropy energy (MAE) as a promising technology on a magnetic device get increasing attention in research activity in the recent years [1], [2]. This is because this technology has many advantages such as lower power consumption, non-volatile, and high speed reading and writing, compared with conventional techniques such as magnetic field induced magnetization switching and spin-current induced torque in magnetic tunnel junction. There are a lot of theoretical investigations and experimental works on modulation of MAE by means of EF in order to understand the mechanism and to demand for a better performance [3]. Several possible origins have been proposed, such as changes in band structure around the Fermi level, which modify the strength of MAE through spin-orbit interaction [4]–[6], Rashba effect [7], [8], orbital hybridization changes [9], changes in $3d$ band population [10], voltage-induced redox reaction [11], the electromigration [12], and the piezoelectric effect [13].

For a practical application, a large perpendicular MAE and large EF effect are needed for the smaller-size magnetic layer element and the accurate dynamic magnetization switching [14]. Among this purpose, many effects were proposed such as a strain effect [15], and an underlayer effect [16]. The underlayer effect becomes important, for example, in the case of intermixing during the fabrication of samples. Nozaki *et al* suggested that an Fe/Cr intermixing in the Cr/Fe/MgO system possibly happens when an annealing is used during the deposition process. They discussed that the annealing make a large effect in the quantities of the perpendicular magnetic anisotropy (PMA), saturation magnetization, and voltage control magnetic anisotropy (VCMA). Later, such intermixing in the same system was clearly observed by using the conversion electron Mössbauer spectroscopy (CEMS) measurement [17].

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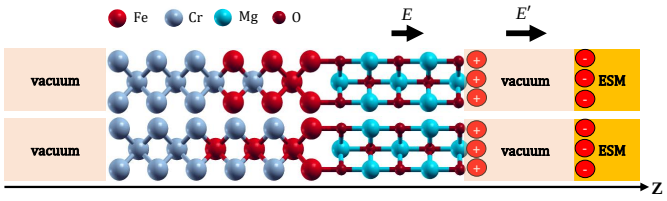

Fig. 1. Schematic diagram of the computational model system A (top) and system B (bottom). The black arrows with label E and E' indicate the electric field in MgO and the vacuum respectively.

Motivated by the experimental results, in this paper, we systematically investigated EF induced MAE in Cr/Fe/MgO systems by introducing Fe/Cr intermixing. The enhancement in MAE and an opposite sign in the EF coefficient by changing the thickness of intermixing layers were observed. We discussed such origin of unique behavior related to significant changes in the electronic structure. Furthermore, we calculated the MAE and EF control MAE by a strain engineering and discussed for an improvement in device applications.

II. Interface Models and Computational Details

We systematically investigated EF effect in Fe/MgO interface systems with Cr underlayer by introducing the interchange of Cr and Fe layers. Our model using slab system, vacuum (0.79 nm)/Cr (6ML)/Fe (1ML)/Cr (1ML)/Fe (3ML)/MgO (5ML)/vacuum (0.79 nm) (system A) and vacuum (0.79 nm)/Cr (5ML)/Fe (1ML)/Cr (1ML)/Fe (1ML)/Cr (1ML)/Fe (2ML)/MgO (5ML)/vacuum (0.79 nm) (system B) as shown in Fig. 1. We carried out first-principles electronic structure calculations [18] which employ fully relativistic and scalar

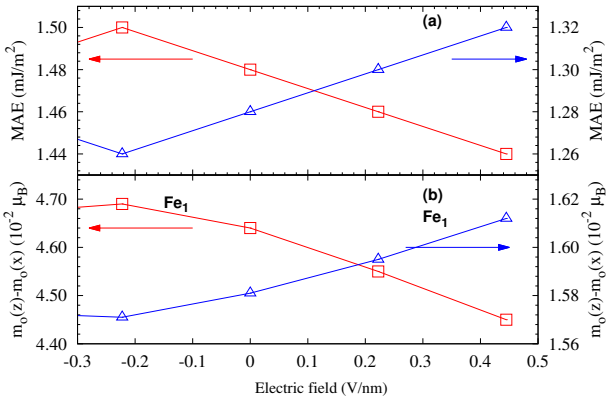

Fig. 2. (a) MAE and (b) orbital moment difference as EF dependence in system A (blue triangles) and system B (red squares).

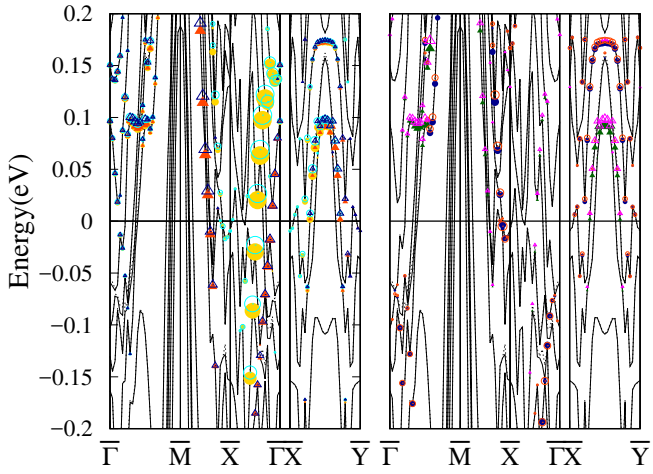

Fig. 3. Band dispersions for zero EF (solid curves) and 0.436 V/nm (dotted curves) system A. In zero EF (0.436 V/nm), the predominant components of Fe 3d orbitals (d_{xz}, d_{yz}, $d_{x^2-y^2}$, and d_{xy}) for minority spin-states are marked as, orange-red filled (dark-blue empty) triangles, gold filled (cyan empty) circles, dark-green filled (magenta empty) triangles, and dark-blue (orange-red empty) circles, respectively.

relativistic ultrasoft pseudopotentials and a plane wave basis by using the generalized gradient approximation (GGA) for the exchange-correlation energy [19]. The magnetic anisotropy energy (MAE) was calculated from the total energy difference between in-plane magnetization ([100] direction) and out-of-plane magnetization ([001] direction), MAE = E[100]-E[001]. We used a 32×32×1 **k**-mesh for both MAE and EF calculations. Using the scalar-relativistic level computation with a 24×24×1 **k**-mesh, we induced structural relaxation while keeping both the in-plane lattice constant and the atomic coordinates of O(3). To apply an EF, we used the effective screening medium (ESM) method [20]. To obtain the EF inside the MgO layer, we took into account the dielectric constant $\varepsilon_{\rm r}$ (9.8 for MgO) [21].

III. RESULTS AND DISCUSSION

A. MAE and EF effect on MAE in Fe/Cr intermixing

The MAE for system A and B in zero EF are 1.28 mJ/m^2 and 1.48 mJ/m^2, respectively. These values were largely enhanced, compared to the system which consists of Cr(6ML)/Fe(4ML)/MgO(5ML) (MAE = 0.59 mJ/m^2 without introduce Fe/Cr intermixing) [22]. In addition, this PMA value is comparable to the experimental result [14] after subtracting the shape anisotropy contribution, K_dt = 0.690 mJ/m^2. K_dt estimated by using continuum model, $K_dt_{Fe} = -\mu_0 M_s^2/2$, where μ_0 is the permeability of vacuum and M_s is saturation magnetization [23]. In this estimation, we used M_s = 0.0785 memu/cm^2 extracted from experimental data for t_{Fe} = 0.56 nm (1ML ≈ 0.14 nm) [14].

By imposed positive EF (correspond to electron depletion in experimental measurement), we observe a different behavior in changes of MAE as shown in Fig. 2(a). MAE is increase (decrease) as EF increase for system A and B respectively. This behavior lead to an opposite sign in EF coefficient (γ) i.e +89 fJ/Vm and -92 fJ/Vm. This result qualitatively agree with an orbital moment calculation of Fe/MgO interface (Fe_1) as shown in Fig. 2(b). MAE is comparable to the orbital moment as in the Bruno expression, MAE = $\xi\Delta m_o/4\mu_B$ where Δm_o = m_o[001]-m_o[100] (difference between the out-of plane and in-plane orbital moment), μ_B is Bohr magnetons and ξ is the spin orbit coupling (SOC) constant.

In order to investigate the origin of enhancement in the PMA and the opposite sign of γ, we calculate band structure both in zero and under EF. Fig. 3 is a partial band structure minority spin-states of d-orbital Fe at the interface (Fe1). At first, we discuss the enhancement of the PMA can be related to the changes of the state d_{xz} and d_{yz} component at $\overline{\Gamma}$ point which shifted up to the higher energy for system A and become split in system B. Our previous result [22] at $\overline{\Gamma}$ point shows the negative contribution to the MAE (see Fig. 4(c) in Ref. [22]). By considering second-order perturbation theory, MAE can be expressed as [24]

$$\mathrm{MAE} \approx \xi^2 \sum_{\mathbf{k}o,u} \frac{|\langle \mathbf{k}_o|\hat{\ell}_z|\mathbf{k}_u\rangle|^2 - |\langle \mathbf{k}_o|\hat{\ell}_x|\mathbf{k}_u\rangle|^2}{\varepsilon_{\mathbf{k}u} - \varepsilon_{\mathbf{k}o}}, \qquad (1)$$

where $\mathbf{k}_o$ and $\mathbf{k}_u$ indicate the occupied and unoccupied states with the wave vector $\mathbf{k}$ and $\hat{\ell}_z$, $\hat{\ell}_x$ are the angular momentum operators. $\varepsilon_{\mathbf{k}u}$ and $\varepsilon_{\mathbf{k}o}$ indicate the energy of unoccupied and occupied states. The SOC between occupied and unoccupied state with the same (different) in magnetic quantum number through to the $\hat{\ell}_z$ ($\hat{\ell}_x$ and $\hat{\ell}_y$) operators give positive (negative) contribution to MAE. Based on Eq. (1), we discuss that the negative contribution to the MAE comes from the SOCs of $\langle xz||xy\rangle$ and $\langle yz||x^2-y^2\rangle$ through the $\hat{\ell}_x$ operator. With the changes of d-orbital states at $\overline{\Gamma}$ point, their contribution may decrease and simultaneously increase the SOCs of $\langle yz||xz\rangle$ and $\langle xy||x^2-y^2\rangle$ through the $\hat{\ell}_z$ operator. As a result, finally the MAE may be enhanced.

At second, the applied EF can modulate the electronic structure, especially near the Fermi level, which mainly contributes to the increase and decrease of MAE according to Eq. (1). In the case of intermixing [Fe/Cr]n (n=1), the electronic structure slightly changes compared to the system without intermixing. In this system, the positive sign of γ can be explained as follows. At $\overline{\rm X}$-$\overline{\rm Y}$ line, $d_{x^2-y^2}$, d_{xz}, and d_{yz} after imposing EF goes up to the higher energy and become unoccupied.

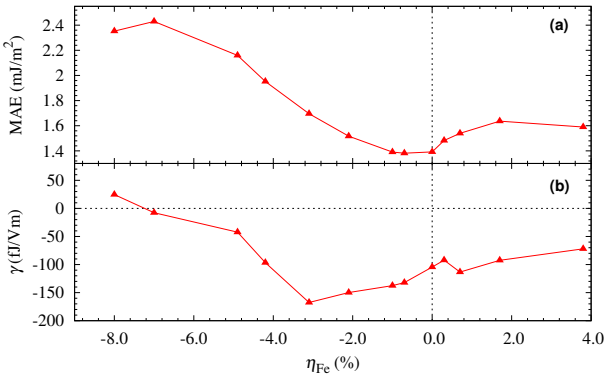

Fig. 4. (a) MAE and (b) electric-field-induce MAE coefficient (γ) in system B as strain dependence.

These changes may increase the SOCs of $\langle xy||x^2-y^2\rangle$ and $\langle yz||xz\rangle$ through to the $\hat{\ell}_z$ operator and thus increase the MAE. Furthermore, at $\overline{\text{X}}$-$\overline{\Gamma}$ line, d_{yz} because also goes up to the higher energy and may increase the SOC of $\langle yz||xz\rangle$ through to the $\hat{\ell}_z$ operator and thus also increase the MAE.

Next, in the case of intermixing [Fe/Cr]n (n=2), the electronic structure significantly changes compared to (n=1). All d-orbital components become more localized near the Fermi level (not shown here). The typical changes can be seen as in the Fig. 5(c). This change may lead to the sign changes in γ. In detail, at $\overline{\text{X}}$-$\overline{\text{Y}}$ line, after imposing EF, states $d_{x^2-y^2}$, d_{xz}, d_{yz} goes upward and become unoccupied. This change may decrease the SOCs of $\langle xy||x^2-y^2\rangle$ and $\langle yz||xz\rangle$) through to the $\hat{\ell}_z$ operator and thus decrease the MAE. Next, at $\overline{\text{X}}$-$\overline{\Gamma}$ line, when d_{yz} upward to the higher energy and become unoccupied, then SOC $\langle yz||xz\rangle$ may decrease and contribute the decrease of MAE through $\hat{\ell}_z$ operator.

The substantial rearrangement of electronic structure for [Fe/Cr]n (n=1 and 2) may be related to the proximity effect of Fe and Cr. The proximity effect here is assosiated with two mechanisms. At first, the hybridization with Cr, Fe d-states are shifted to the lower energy since Cr d-states are located in the higher energy [25]. At second, electrons can transfer from Cr to Fe atoms due to a smaller electronegativity of Cr. Consequently, the 3d orbital on the Fe of Fe/MgO interface may increase. This increase strongly depends on the vicinity of Cr next to Fe/MgO interface. In addition, we also notice

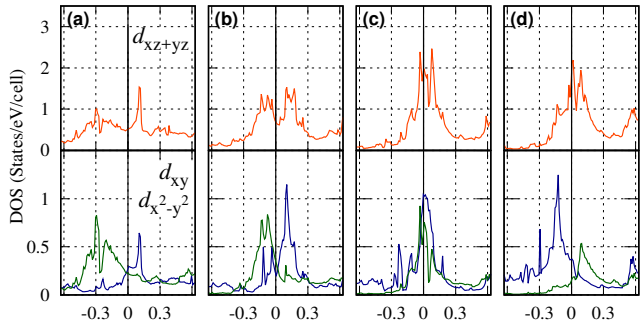

Fig. 5. Projected density of states (PDOS) in system B for (a) η_{Fe}=−8.0%, (b) η_{Fe}=−3.1%, (c) η_{Fe}=0.0%, and (d) η_{Fe}=3.8%, respectively. The green (blue) specifies $d_{x^2-y^2}$ (d_{xy}).

that the number of electrons (NOE) in d-orbital for system B is increased by 0.052 from that for system A. This larger NOE may be an origin of sign change in γ. Experimentally, an opposite sign in voltage control magnetic anisotropy (VCMA) was also observed between Ta and Ru underlayers. Discussion of this opposite sign was related to a different spin-orbit coupling in the underlayer, a difference in crystallinity etc., but the origin is still an open question [26].

B. MAE and EF modulation in MAE as strain dependence

For further exploration at vicinity of the Fermi level, we calculate MAE as strain dependence for system B, as shown in Fig. 4(a). In this work, the variation of strain is taken in the range of -8.0% to 3.8% for the ratio with respect to Fe lattice constant (2.87Å). As a result, MAE increases with increasing tensile strain (increase in lattice constant) and increasing compressive strain (reduce in lattice constant) with the maximum value of 2.43 mJ/m^2. This MAE is strongly related to the SOCs of d-orbital component on the interface Fe, especially those of eigen-states near the Fermi level. The behavior is shown in the partial DOS (Fig. 5). By increasing compressive strain, $d_{x^2-y^2}$ and part of d_{xz}, d_{yz} gradually shift to the lower energy and become below the Fermi level while d_{xy} and part of d_{xz}, d_{yz} stay above the Fermi level (Fig. 5(a) and 5(b)). This kind of coupling may increase the MAE due to SOC of $\langle xy||x^2-y^2\rangle$ and $\langle yz||xz\rangle$) through to the $\hat{\ell}_z$ operator. These changes mainly appear at $\overline{\text{X}}$-$\overline{\text{Y}}$ line (not shown). On the other hand, by increasing tensile strain such mechanism also appears, but it is a reverse. At $\overline{\text{X}}$-$\overline{\text{Y}}$ line, d_{xy} and part of d_{xz}, d_{yz}, are also push down to the lower energy and become occupied while $d_{x^2-y^2}$ and part of d_{xz}, d_{yz} stay above the Fermi level (Fig. 5(d)). Again, such coupling may also increase the MAE through to $\hat{\ell}_z$ operator as in the previous one.

The total number of electrons (NOE) d-orbital as a strain dependence is shown in Fig. 6(a). Generally, the total NOE of d-orbital decrease (increase) by increasing tensile (compressive) strain. In more detail, the NOE of each d-orbital component is shown in Fig. 6(b). The behavior of total NOE as a strain dependence is related to NOE of d_{yz+xz} and $d_{x^2-y^2}$. The increase of in-plane lattice constant may reduce the interlayer distance along z-direction. This mechanism may enhance the hybridization between Fe, resulting in a strong bonding which leads to the delocalization of electrons and finally reduces the NOE of d-orbital.

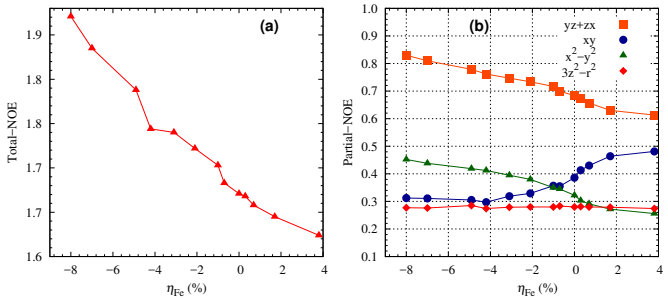

Fig. 6. Number of 3d electrons (NOE) on the Fe/MgO interface as a strain dependence, (a) total-NOE and (b) partial-NOE of each orbital.

Furthermore, the electric field (EF) coefficient (γ) as strain dependence is shown in Fig. 4(b). The maximum absolute value of γ is 170 fJ/Vm at $\eta_{\mathrm{Fe}} = -3.1\%$. This larger value can be related to a large amount of d-orbital states around the Fermi level. As shown in Fig. 5(b), at zero EF, $d_{x^2-y^2}$ and part of d_{xz}, d_{yz} are occupied and form states just at the Fermi level. After applying EF, these states are shifted to the higher energy and become unoccupied. This change may reduce the SOCs of $\langle xy||x^2-y^2\rangle$ and $\langle yz||xz\rangle$ through to the $\hat{\ell}_z$ operator. Due to this reduction the MAE may reduce significantly, resulting in a larger MAE change. However, the values obtained in the present work are not enough for an electrical control of magnetism ($\sim$1pJ/Vm) in a device application. For further enhancements in VCMA, several scenarios have been discussed as well as the present strain engineering [15]; elements with large SOCs [16], barrier (insulating) materials with a high dielectric constant, etc. As an emerging one, there may be a combination with antifferromagnetic materials [3] whose MAE is sensitive to an external perturbation such as strain.

IV. CONCLUSIONS

We demonstrated the opposite sign in the VCMA by introducing the intermixing at the underlayer in the Cr/Fe/MgO system. This intermixing leads to the significant changes at the electronic structure in the Fe/MgO interface. We found the orbital reconstruction originating from a proximity effect of the Cr/Fe interface. The analysis in the modulation of d-orbital component in band dispersion near the Fermi level may explain the opposite sign of γ along the second-order perturbation theory. This sign changes also qualitatively agree with the data of orbital moments. This result provides a new possible degree of freedom for EF control in MAE as underlayer configuration. Furthermore, the enhancements in MAE and VCMA may be realized via strain engineering. This indicates that there is a new possibility to introduce other elements which have a lattice constant lower than that of Cr for the buffer layer.

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