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Finite Electric Field Effects in the Large Perpendicular Magnetic Anisotropy Surface Pt/Fe/Pt(001): A First-Principles Study

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We investigate crystalline magnetic anisotropy in the electric field (EF) for the FePt surface which has a large perpendicular anisotropy, by means of the first-principles approach. Anisotropy is reduced linearly with respect to the inward EF, associated with the induced spin density around the Fe layer. Although the magnetic anisotropy energy (MAE) density reveals large variation around the atoms, the intrinsic contribution to the MAE is found to mainly come from the Fe layer. The surface without the capping Pt layer also shows similar linear dependence.

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Magnetoelectric properties in the solid state are attractive for spintronics applications. Through spin-orbit interaction (SOI) magnetic and electric properties are connected and, consequently, the electric field (EF) allows us to manipulate magnetic properties [1] and the magnetic field could control the electric polarization of materials [2]. Such properties may be allowed in the system which loses time-reversal and space-inversion symmetries, e.g., surface magnetization systems. One of the important problems is to control magnetic anisotropy with the voltage or the EF. The EF-induced variation of coercivity has been observed in the ferromagnetic semiconductor [3] and the large perpendicular magnetization metallic surface (FePt and FePd thin layers) [4]. Strong magnetic anisotropy is necessary in the nanoscale device so as not to loose magnetic memory by thermal fluctuation, but at the same time it makes the reversal of magnetization difficult. The large experimental observation of EF effect on coercivity has been reported [5]. The direct estimation of magnetic anisotropy energy (MAE) was performed for the thin film, Au/Fe/MgO [6]. Recent theoretical works on magnetoelectric properties in the thin iron films have explained the variation of MAE [7,8], based only on a simplified Bruno's relation (relationship between the MAE and the atomic orbital magnetic moments) [9].

In order to obtain a built-up technology, the stable theoretical background for the EF effect is required in the basis of realistic electronic structures. The present theoretical work shows that the surface accumulated charge modifies the strength of magnetic anisotropy through the modulation of electronic state at the magnetic layer. We will discuss origins of the change and intrinsic contributions to the MAE.

We have carried out first-principles electronic structure calculations [10] which employ ultrasoft pseudopotentials [11] and plane wave basis. Except for imposing the EF, the details about the method and the models are the same as in the previous study for Pt/Fe/Pt(001) and Fe/Pt(001) in no EF [12]. These systems have four atomic Pt layers for the substrate and the atomic positions of the three bottom layers were fixed to the appropriate values of the bulk fcc Pt. The other atoms were relaxed using the calculated atomic forces under the zero EF. All the atomic positions were fixed for finite EFs in MAE calculations. The atomic displacements induced by the EF may be a future problem for magnetoelectric physics and MAE estimation. In order to impose the EF, we have applied the scheme of effective screening medium (ESM) developed by Otani and Sugino [13]. As shown in Fig. 1(a), the ESM of ideal conductor

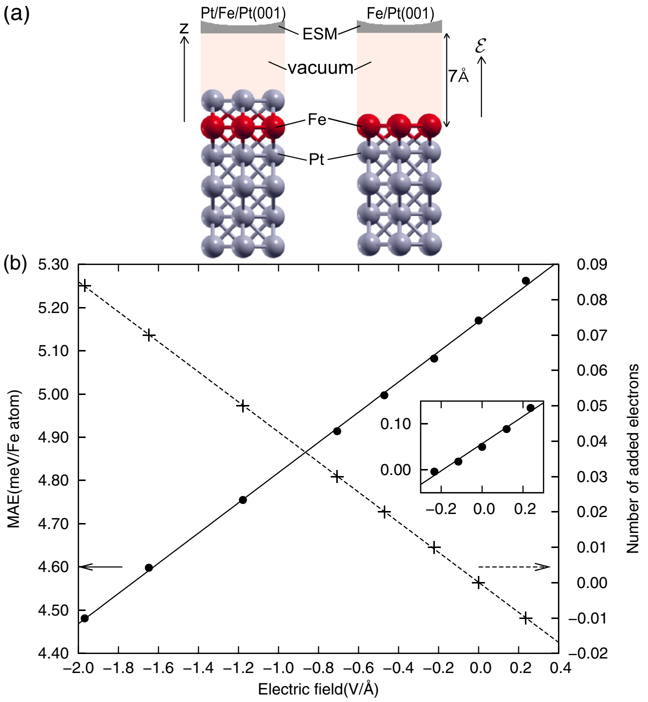

FIG. 1 (color online). (a) Schematic diagram of the computational models. (b) Magnetic anisotropy energies (MAEs) (solid dots) and the number of added electrons (crosses) as a function of the electric field for Pt/Fe/Pt(001). The inset shows the MAEs as a function of the electric field for Fe/Pt(001). The lines are obtained by the least squares fit to the set of data.

was placed away from the Fe layer by 7.0 Å. Some tiny number of electrons was added in the slab for induction of the EF and at the same time induction of the counterpart charge at the ESM surface. The strength of EF was estimated at the front of ESM.

The MAE was estimated from the total energy difference between in-plane magnetization ([100] direction) and out-of-plane (perpendicular) magnetization ([001] direction): MAE $= E_{\mathrm{tot}}^{[100]} - E_{\mathrm{tot}}^{[001]}$. In the present work the MAE density $D(\mathbf{r})$ has been introduced to understand the local contribution of MAE from a coarse-grain region of real space. The total energy $E_{\mathrm{tot}}^{\mathbf{m}}$, where $\mathbf{m}$ specifies the magnetization direction of system, may be formally specified in any point of real space: $E_{\mathbf{m}}(\mathbf{r})$, where $\int_{\mathrm{cell}} E_{\mathbf{m}}(\mathbf{r}) d\mathbf{r} = E_{\mathrm{tot}}^{\mathbf{m}}$. The atomic contribution in the total energy (nonlocal part from the pseudopotential, etc.) was redefined as a Gaussian form function centered at the atomic position. The MAE density was defined by $D(\mathbf{r}) = E_{[100]}(\mathbf{r}) - E_{[001]}(\mathbf{r})$ and the MAE is alternatively obtained by $\int_{\mathrm{cell}} D(\mathbf{r}) d\mathbf{r}$. The atomic contributions of MAE were estimated by integrating $D(\mathbf{r})$ within the atomic sphere with the radius of 1.3 Å and the layer contributions within the layer with the plane boundaries determined with the midpoint of atomic coordinates along the c direction or the surface normal. The z-dependent MAE density $\Delta(z)$ was obtained by summing $D(\mathbf{r})$ up within the in-plane unit cell in the fixed plane normal to the surface. Further, we introduced another integrated MAE density: $T(z) = \int_{-\infty}^{z} \Delta(z') dz'$. This function helps us to capture the feature of $\Delta(z)$. The functions introduced above were calculated at a given EF ($\mathcal{E}$): $D(\mathbf{r}, \mathcal{E})$, $\Delta(z, \mathcal{E})$, and $T(z, \mathcal{E})$.

The bulk $L1_0$-FePt has a magnetic anisotropy along the c direction. The total MAE is divided to contribution of each atom (1.96 meV and -0.01 meV in Fe and Pt atoms, respectively) and the interstitial region (0.67 meV/f.u.) [14,15]. This total MAE is also partitioned to the Fe and Pt layers along the c direction, resulting in 2.83 meV and -0.21 meV in Fe and Pt layers, respectively. These results, though the values associated with Pt are small and negative, have never expressed a minor contribution to magnetic anisotropy from Pt atoms. The intra-atomic spacial variation around Pt atoms is remarkable, reflected from a large spin-orbit interaction on Pt atoms and the hybridization of Pt $5d$ with Fe $3d$ are responsible for the large magnetic anisotropy of such systems [16]. The spacial partition on MAE becomes very interesting in the surface systems and also under the EF, because the potential gradient against electrons is changed and the electronic structure is modulated, which results in the modulation of effective spin-orbit parameter [17].

In Pt/Fe/Pt(001), the MAE contributes mainly from Fe layer at zero field (5.50 meV/Fe), amounting to 121% of the total (5.21 meV/Fe). The main negative contribution comes from the capping Pt layer (-0.85 meV/Fe). After imposing the inward EF the MAE decreases, associated with an increase of the number of added electrons. The similar decrease has been reported in the literature [4], where the decrease of MAE speculatively coincides with the bandfilling in the $L1_0$-FePt [18]. Figure 1(b) presents the EF dependence of MAEs in Pt/Fe/Pt(001), associated with the number of added electrons in the unit cell. The method for imposing EFs [13] almost does not affect ($\sim$0.01 meV/Fe) the MAE at zero field, compared with the previous estimation with the simple periodic slab approach [12]. The dependence of the EF on the number of added electrons is almost linear. The slope rate corresponds to the dielectric constant for vacuum (ε_0): $\sim 1.00\varepsilon_0$. The decrease rate of MAE with respect to the inward EF is estimated to be 0.35 meV per Fe atom per V/Å, corresponding to the surface MAE of 72 fJ/V m. This rate is larger than the previous theoretical estimation for the metallic surface of iron by the factor of 3.8 ($\sim$19 fJ/V m) [8]. Moreover, although the substrate of system is different, this slope could explain a partial contribution of the change of MAE by voltage in the experimental measurement [6].

In Figs. 2(a)–2(c) the EF-induced MAE densities, $\Delta(z, \mathcal{E}_1) - \Delta(z, 0)$, $T(z, \mathcal{E}_1) - T(z, 0)$, and $D(\mathbf{r}, \mathcal{E}_1) - D(\mathbf{r}, 0)$, where $\mathcal{E}_1 = -1.97$ V/Å, are shown along z direction in Pt/Fe/Pt(001). In these figures, the MAE density has large strengths around Pt atoms, which reflects the large SOI at them. However, such contributions to the MAE seem to cancel out around Pt atoms and, as shown in Fig. 2(b), the intrinsic contribution to the total induced variation on MAE is raised around the Fe layer. This indicates that the local electronic structure centered at the Fe layer is intrinsically important for the change of MAE.

To see the relationship between the variation of MAE and the EF in more detail, we have calculated induced spin density, energy-dependent density of states for five $3d$ angular-dependent orbitals on Fe atom, and orbital-

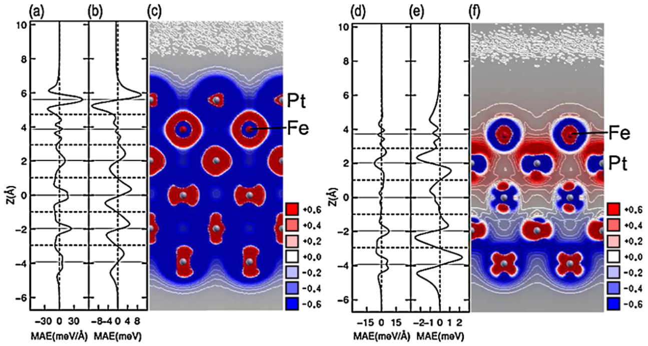

FIG. 2 (color online). Electric field change of the magnetic anisotropy energy (MAE) densities along z coordinate and the contour (meV/Å^3) maps, (a)–(c) for Pt/Fe/Pt(001), and (d)–(f) for Fe/Pt(001). The horizontal solid and dashed lines in (a),(b), (d),(e) indicate the atomic positions and the layer's boundaries, respectively, for better visualization. The maps, (c) and (f), are shown in the (110) plane on the Fe (red or dark gray ball) and Pt (gray ball) atoms.

specified band dispersions [12]. Figures 3(a) and 3(b) show the induced majority- and minority-spin densities along the z direction and the induced spin density map, respectively, at $\mathcal{E} = -1.97$ V/Å in Pt/Fe/Pt(001). At Fe the minority-spin density is induced and this induction is found to result in a partial cancellation of the increase of $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ components against the decrease of d_{xz} and d_{yz}. The latter is associated with the charge accumulation at the outside of the capping layer through the orbital hybridization between Fe $3d$ and Pt $5d$, which implies a subtle bonding reduction. As a result, the d_{xz} and d_{yz} components grow just above the Fermi level. These EF modulations in electronic structure around the Fermi level can be related with the decrease of MAE by using the second order perturbative consideration [19];

$$\mathrm{MAE} \propto \sum_{\mathbf{k}} \sum_{o,u} \frac{|\langle \mathbf{k}o|\ell_z|\mathbf{k}u\rangle|^2 - |\langle \mathbf{k}o|\ell_x|\mathbf{k}u\rangle|^2}{\varepsilon_{\mathbf{k}u} - \varepsilon_{\mathbf{k}o}}, \tag{1}$$

where $\mathbf{k}o$ and $\mathbf{k}u$ specify the occupied and unoccupied states with the wave vector $\mathbf{k}$ and $\ell_\alpha (\alpha = x, z)$ the angular momentum operators. The EF modulation mentioned above increases the couplings between occupied and unoccupied states (couplings of $\langle 3z^2 - r^2 \parallel yz\rangle$ and $\langle yz \parallel x^2 - y^2\rangle$) through the ℓ_x operator and, thus, reduces the MAE [19].

Another surface Fe/Pt(001) also shows a similar linear change of MAE with respect to the EF [see the inset in Fig. 1(b)]. The comparisons with Pt/Fe/Pt(001) are tabulated in Table I. Although both MAEs at $\mathcal{E} = 0$ are largely different, their slope rates are positive and similar to each other. This does not mean a same origin in electronic structure for the EF variations. As shown in Figs. 2(d)–2(f) and 3(c) and 3(d), the induced MAE density and the induced spin density at $\mathcal{E} = -0.23$ V/Å completely differ from those of Pt/Fe/Pt(001) around the Fe layer. At Fe the minority-spin density, except for s and $d_{3z^2-r^2}$ components, is reduced significantly, avoiding the Coulomb repulsion with the largely induced electron at outside of the Fe layer. By analyzing the densities of states and the band dispersions along with Eq. (1), the reduced MAE against the inward EF may mainly come from a decrease of the couplings between occupied and unoccupied states of d_{xz} and d_{yz} through the ℓ_z operator.

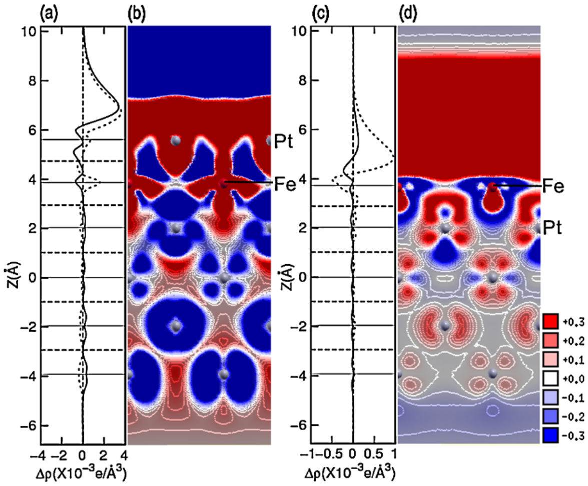

FIG. 3 (color online). The induced majority (solid curves) and minority (dashed curves) spin charge densities along the z coordinate and the contour maps of induced spin densities ($\times 10^{-3}\ e/\text{Å}^3$) (a),(b) for Pt/Fe/Pt(001) and (c),(d) for Fe/Pt(001). The magnetization direction used for the figure drawing is perpendicular to the surface plane. See the caption at Fig. 2 for other explanations.

In Table I, the spin and orbital moments are reported. These quantities change linearly with the EF in Pt/Fe/Pt(001). One would explain the MAE from the orbital magnetic moments, while it is not probable that the simplified Bruno's relation applies to the FePt alloy [see Eq. (9) in [14]] without the spin flip contribution [9]. This is because the Pt does not have any large exchange splitting. As implied by the difference of atomic orbital magnetic moments on Fe and Pt atoms in Table I, the MAE may be supposed to mainly come from the Pt atoms. This picture is in contradiction with the feature obtained from the MAE density (Fig. 2). In this context, to give a reasonable explanation in the relation with the orbital magnetic moment and the MAE, the application of a general Bruno's relation is required, accompanied with the spin flip contribution and the interstitial (interatomic) contribution to the MAE.

The exposure of the Fe layer to vacuum in Fe/Pt(001) causes the drastic change in the MAE as well as the electronic structure of the Fe layer. Even when a dielectric material is introduced instead of the vacuum, the differ-

TABLE I. Comparison of magnetoelectric properties in Pt/Fe/Pt(001) and Fe/Pt(001); magnetic anisotropy energies (MAEs) at zero field and their gradients with respect to the electric field ($\mathcal{E}$), the spin magnetic moment (SMM) from the surface layers (3 and 2 layers, respectively) in the [001] magnetization, and the difference of atomic orbitals magnetic moments (DOMM) between the [001] and [100] magnetizations, $M_{\mathrm{orb}}[001] - M_{\mathrm{orb}}[100]$.

	Pt/Fe/Pt(001)	Fe/Pt(001)
MAE at $\mathcal{E} = 0$	5.21 (11)[a]	0.05 (0.11)[a]
MAE slope rate	0.35 (72)[b]	0.30 (62)[b]
SMM at $\mathcal{E} = 0$	3.72[c]	3.45[c]
SMM slope rate	0.0065(0.99)[d]	0.043 (6.47)[d]
Fe DOMM at $\mathcal{E} = 0$	0.0080[c]	−0.0066[c]
Fe DOMM slope rate	−0.0037 (−0.56)[d]	
Pt(c) DOMM at $\mathcal{E} = 0$	−0.0417[c]	
Pt(c) DOMM slope rate	−0.0024 (−0.36)[d]	

[a] In meV/Fe (mJ/m^2).
[b] In meV/Fe per V/Å (fJ/V m).
[c] In μ_B.
[d] In μ_B per V/Å(10^{-18} Gm^2/V).

ences mentioned above between Pt/Fe/Pt(001) and Fe/Pt(001) may still be present. The increase of electric constant in the dielectric material increases the induced charge at the interface with the metal under a given EF. Indeed, the interface MgO(001)/Pt/Fe/Pt(001) shows a larger slope rate in the MAE variation with respect to the EF. The different substrate, e.g., Au substrate effectively lifts up the Fermi level with respect to the Fe 3*d* component, which implies a reduction of perpendicular anisotropy compared with the Pt substrate. Our realistic model calculation artificially contains the interactions between the surfaces in the slab. Such interactions may be canceled partially by increasing the thickness of substrates, due to screening effects of the metal. Nevertheless, any major intrinsic contribution to the MAE has not been observed in the present study.

Imposing the EF, the number of electrons changes in a few layers of the surface due to a screening effect of metal, as shown Figs. 3(a) and 3(c). This feature should be realized also in the experiment [4]. If the change of coercivity is assumed to be attributed to the one or two magnetic layers of the metal surface in the experiment, the MAE of these layers could reduce by $10 \sim 30\%$ for the EF of -0.03 V/Å. This reference to the experiment provides a good agreement with our decrease of MAE [13% in Pt/Fe/Pt(001)] by the EF of -0.030 V/Å which is scaled by the dielectric constant of the experimental substrate on metal surface (-1.97 V/Å on vacuum).

In summary, we have studied the EF dependence of MAE for the large perpendicular magnetic anisotropy surface system and the related system without the capping layer. MAE linearly decreases with the inward EF in both Pt/Fe/Pt(001) and Fe/Pt(001). The slopes of MAE vs EF are similar for both systems, though the origins of variations are different in accordance with the difference of the electronic structure of systems. By analysis of the induced MAE density, the large variation around Pt atoms was revealed and the intrinsic contribution to MAE was verified to mainly come from the Fe layer. The analysis of MAE density provides a promising tool for pursuing the spacial contribution of nanoscale structures, regardless of the knowledge of orbital magnetic moments. The present study indicates that the relative modification in the electron filling of each 3*d* orbital by the EF, resulting in the accumulated charge at the magnetic layer, causes the variation of MAE.

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