Finite electric field effects in the large perpendicular magnetic anisotropy surface Pt/Fe/Pt(001)

Masahito Tsujikawa\textsuperscript{1} and Tatsuki Oda\textsuperscript{2}

\textsuperscript{1}Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa 920-1192, Japan
\textsuperscript{2}Institute of Science and Engineering, Kanazawa University, Kanazawa 920-1192, Japan

(Dated: May 1, 2009)

Abstract

We have investigated crystalline magnetic anisotropy in the electric field (EF) for the Fe-Pt surface which have a large perpendicular anisotropy, by means of the first-principles approach. The 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 the large variation around the atoms, the intrinsic contribution to the MAE is found to mainly come from the Fe layer.
Magnetoelectric properties in the solid state are attractive for the spintronics applications. Through the spin-orbit interaction (SOI) the magnetic and electric properties are connected and consequently, the electric field (EF) allows us to manipulate the magnetic properties and the magnetic field could control the electric polarization of materials. Such properties may be allowed in the system which looses the time-reversal and space-inversion symmetries, e.g., surface magnetization systems. One of the important problems is to control the magnetic anisotropy with the voltage or the EF. The EF induced variation of coercivity has been observed in the ferromagnetic semiconductor and the large perpendicular magnetization metallic surface (FePt and FePd thin layers). The strength of magnetic anisotropy needs in the nanoscale device so as not to loose the magnetic memory by the thermal fluctuation and, meanwhile, makes difficulties in reversing the magnetization. The large experimental observation of EF effect on coercivity has been reported. The direct estimation of magnetic anisotropy energy (MAE) was performed for the thin film, Au/Fe/MgO. Recent theoretical works on magnetoelectric properties in the thin iron films have explained the variation of MAE, based only on a simplified Bruno’s relation (relationship between the MAE and the atomic orbital magnetic moments).

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 which employ ultrasoft pseudopotentials and planewave 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) in no EF. 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 the magnetoelectric physics and the MAE estimation. In order to impose the EF, we have applied the scheme of effective screening medium (ESM) developed by Otani and Sugino. In the present work, the ideal conductor 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 of the system with the in-plane magnetization ([100] direction) with respect to that of the out-of-plane (perpendicular) magnetization ([001] direction). In the present work the MAE density, \( D(r) \), has been introduced to understand the local contribution of MAE from a coarse-grain region of real space. The total energy \( E_{\text{tot}}^m \), where \( m \) specifies the magnetization direction of system, may formally be divided to the local point in real space; \( E_m(r) \), where \( \int_{\text{cell}} E_m(r)dr = E_{\text{tot}}^m \). The atomic contribution in the total energy (non-local part from the pseudopotential, etc.) was redefined as a Gaussian form function centered at the atomic position. The MAE density was defined by \( D(r) = E_{[100]}(r) - E_{[001]}(r) \) and the MAE is alternatively obtained by \( \int_{\text{cell}} D(r)dr \). The atomic contributions of MAE were estimated by integrating \( D(r) \) 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 \( D(r) \) 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 \( (\mathcal{E}) \); \( D(r, \mathcal{E}) \), \( \Delta(z, \mathcal{E}) \), 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 5\( d \) with Fe 3\( d \) are responsible to 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, thus, which will result 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),
FIG. 1: Magnetic anisotropy energies (MAEs) (circles) and the number of added electrons (crosses) as a function of the electric field for Pt/Fe/Pt(001). The lines are obtained by the least squares fit to the set of data.

amounting to 121% of the total (5.21 meV/Fe). The main negative contribution comes from the capping Pt layer (−0.85 meV/Fe). Imposing the inward EF the MAE decreases, associated with 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 L1₀-FePt [18]. Figure 1 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 unchanged (∼0.01meV/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. This slope rate corresponds to the dielectric constant for vacuum ($\varepsilon_0$; ∼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/A, corresponding to the surface MAE of 72 fJ/Vm. This rate is larger than the previous theoretical estimation for the metallic surface of iron by the factor of 3.8 (∼19 fJ/Vm) [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)-(c) the EF-induced MAE densities, $\Delta(z, E_1) - \Delta(z, 0)$, $T(z, E_1) - T(z, 0)$, and $D(r, E_1) - D(r, 0)$, where $E_1 = -1.97$V/A, 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 details, we have calculated the induced spin density, the energy-dependent density of states for five 3d angular-dependent orbitals on Fe atom, and the orbital-specified band dispersions [12]. Figures 3(a) and (b) show the induced majority- and minority-spin densities along z-direction and the induced spin density map, respectively, at $E = -1.97V/Å$ 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 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.
FIG. 3: (color online). The induced majority- (solid curves) and minority- (dashed curves) spin charge densities along z-coordinate and the contour maps of induced spin densities ($\times10^{-3}e/\text{Å}^3$) (a)(b) for Pt/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.

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];

$$\text{MAE} \propto \sum_k \sum_{o,u} \frac{|\langle k o|\ell_z|k u \rangle|^2 - |\langle k o|\ell_x|k u \rangle|^2}{\varepsilon_{k u} - \varepsilon_{k o}},$$

where $k o$ and $k u$ specify the occupied and unoccupied states with the wave vector $k$ 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 $\langle 3z^2 - r^2||yz \rangle$ and $\langle yz||x^2 - y^2 \rangle$) through the $\ell_x$ operator and, thus, reduces the MAE [19].

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 (inter-atomic) contribution to the MAE.

Imposing the EF, the number of electrons changes in a few layers of the surface due to a screening effect of metal, as shown Fig. 3(a). 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 ~ 30 % for the EF of $-0.03 V/\text{Å}$. This reference to the experiment provides a good agreement with our decrease of MAE (13 % in Pt/Fe/Pt(001)) by the EF of $-0.030 V/\text{Å}$ which is scaled by the dielectric constant of the experimental substrate on metal surface ($-1.97 V/\text{Å}$ on vacuum).

In summary, we have studied the EF dependence of MAE for the large perpendicular magnetic anisotropy surface system. The MAE linearly decreases with the inward EF in Pt/Fe/Pt(001). By analysis of the induced MAE density, the large variation around Pt atoms was revealed and the intrinsic contribution to the MAE was verified to mainly come from the Fe layer. The analysis of MAE density provides a promising tool for pursuing the

| TABLE I: Magnetoelectric properties in Pt/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 three surface layers in the $[001]$ magnetization, and the difference of atomic orbitals magnetic moments(DOMM) between the $[001]$ and $[100]$ magnetizations, $M_{\text{orb}}[001] - M_{\text{orb}}[100]$. |
|----------------------------------|----------------------------------|
| MAE at $\mathcal{E} = 0$         | 5.21 (11)$^a$                    |
| MAE slope rate                   | 0.35 (72)$^b$                    |
| SMM at $\mathcal{E} = 0$        | 3.72 $^c$                       |
| SMM slope rate                   | 0.0065(0.99) $^d$               |
| Fe DOMM at $\mathcal{E} = 0$    | 0.0080 $^c$                     |
| 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 (J/m²), $^b$ in meV/Fe per V/Å (fJ/Vm),

$^c$ in $\mu_B$, $^d$ in $\mu_B$ per V/Å($10^{-18}$ Gm²/V)
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 3d orbital by the EF, resulting in the accumulated charge at the magnetic layer, causes the variation of MAE.

[1] D. Chiba, M. Sawicki, Y. Nishitani, Y. Nakatani, F. Matsukura, and H. Ohno, Nature 455, 515 (2008).
[2] T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, Nature 426, 55 (2003).
[3] D. Chiba, M. Yamanouchi, F. Matsukura, and H. Ohno, Science 301, 943 (2003).
[4] M. Weisheit, S. Fähler, A. Marty, Y. Souche, C. Poinsignon, D. Givord, Science, 315, 349 (2007).
[5] S. Sahoo, S. Polisetty, C. G. Duan, S. S. Jaswal, E. Y. Tsymbal, and C. Binek, Phys. Rev. B 76, 092108 (2007).
[6] T. Maruyama, Y. Shiota, T. Nozaki, K. Ohta, N. Toda, M. Mizuguchi, A. A. Tulapurkar, T. Shinjo, M. Shiraishi, S. Mizukami, Y. Ando, Y. Suzuki, Nature Nanotech., online publication, 18 Jan (2009).
[7] C. G. Duan, J. P. Velev, R. F. Sabirianov, W. N. Mei, S. S. Jaswal, and E. Y. Tsymbal, Appl. Phys. Lett. 92, 122905 (2008).
[8] C. G. Duan, J. P. Velev, R. F. Sabirianov, Z. Zhu, J. Chu, S. S. Jaswal, and E. Y. Tsymbal, Phys. Rev. Lett, 101, 137201 (2008).
[9] P. Bruno, Phys. Rev. B 39, 865 (1989).
[10] T. Oda, A. Pasquarello and R. Car, Phys. Rev. Lett. 80, 3622 (1998).
[11] K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, Phys. Rev. B 47, 10142 (1993).
[12] For the calculation method, see the references in the following: M. Tsujikawa, A. Hosokawa, and T. Oda, Phys. Rev. B 77, 054413 (2008).
[13] M. Otani and O. Sugino, Phys. Rev. B 73, 115407 (2006).
[14] P. Ravindran, A. Kjekshus, H. Fjellvåg, P. James, L. Nordström, B. Johansson, and O. Eriksson Phys. Rev. B 63, 144409 (2001).
[15] T. Oda and A. Hosokawa, Phys. Rev. B 72, 224428 (2005).
[16] M. Komelj, D. Steiauf and M. Fähnle, Phys. Rev. B 73, 134428 (2006).
[17] M. Nagano, A. Kodama, T. Shishidou, and T. Oguchi, J. Phys.:Condens. Matter 21, 064239 (2009).
[18] G. H. O. Daalderop and P. J. Kelly and M. F. H. Schuurmans, Phys. Rev. B 44, 12054 (1991).
[19] D. S. Wang, R. Wu, and A. J. Freeman, Phys. Rev. B 47, 14932 (1993).