Magnetism and Magnetocrystalline Anisotropy of Co/Fe(001) Surface: A First Principles Study

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Abstract
Recent theoretical calculations predicted that a magnetic thin film composed exclusively of 3d transition metals without heavy metals or rare earth metals can have strong perpendicular magnetocrystalline anisotropy (MCA) in case 3d transition metals such as Fe, Co and Ni layers are arranged appropriately. While previous researches considered only Fe-terminated surfaces and found that Fe/MgO(001) and CoFeB/MgO(001) show strong perpendicular MCA, we investigate magnetism and MCA of Co/Fe(001) film where Co layer is positioned at the surface, by using the first principles calculation. Since the magnetic moments of Co and Fe are enhanced due to strong hybridization between Co and Fe d-bands, Co capped system also should be carefully considered. MCA of Co/Fe(001) is perpendicular to the film surface regardless of film thickness, which implies the surface termination as well as the interface play a crucial role in determining MCA of a system.

Introduction
Materials with strong perpendicular magnetic anisotropy have drawn attention in the field of the storage media such as magnetic random-access memory since it is essential to increase the writing/reading speed and improve memory density [1-9]. To obtain strong perpendicular magnetic anisotropy, 4 and 5d heavy transition metal or rare-earth elements with large spin-orbit coupling have been generally used [10-12]. However, 4 and 5d transition metals as well as rare-earth metals are not abundant, therefore, intense research has been now actively conducted to improve perpendicular magnetic anisotropy without using heavy and rare-earth metals [13,14].

According to several theoretical calculations about magnetic thin film composed of only 3d transition metals, it also can have an enough perpendicular magnetic anisotropy energy in case orbitals of $d_{x^2-y^2}$ and $d_{z^2}$ are placed close to the Fermi level by adjusting film layers [13]. So far, most studies have focused on Fe surface since the strong perpendicular magnetic anisotropy was discovered in Fe/MgO(001) and CoFeB/MgO(001) film systems. However, not only Fe surfaces but also other 3d transition metal surfaces should be carefully considered because extremely induced magnetic moment was predicted in Ni or Co surface with Fe(001) substrate due to a strong band mixing at the interface [15,16].

In present paper, we investigate magnetism and magnetocrystalline anisotropy (MCA) of Co/Fe(001) films with different Fe thickness, from 5- to 17-ML to provide information on how to construct a system to obtain strong magnetic anisotropy in 3d transition metal compounds (Figure 1).

Methods
For density functional theory calculations, we use Vienna ab initio simulation package (VASP) [17-19] and Elk [20] in complementary relations. In the VASP calculation, the pseudopotential is generated by the projected augmented wave method [21]. Generalized gradient approximation is employed for the exchange-correlation potential [22]. A $12\times12\times1$ mesh is used for k summation. For wave function expansion, energy cut-off of 500 eV is used. In the calculation with Elk, the wave functions were expanded into spherical harmonics with an angular momentum quantum number $l_{max}=12$ inside the non-overlapping spheres surrounding the muffin-tin spheres. A plane-wave cutoff of $rgkmax=9$ which sets the maximum length for G+k vectors, was used for the expansion of wavefunctions inside the interstitial regions.

While a film is composed of different thickness of Fe substrate (from 5- to 17-monolayers (MLs)) and 1-ML Co surface as shown...
in Figure 1, in-plane lattice constant of the film is fixed as value of bulk Fe (2.8665 Å), where internal coordinates are fully relaxed within force criteria of 1 meV/Å. To minimize artificial interaction between neighboring slabs, vacuum spacing of 20 Å is adopted between adjacent layers.

Results And Discussions

Atomic structures

We calculate the changes of the interlayer distances after structure optimization as the following relationship, \( \Delta d = d_{j-i} - d_0 \), where \( d_0 \) denotes the layer distance of the bulk Fe. From the calculated results depicted in Figure 2, we can infer that the interlayer distance decreases on the surface but increases in the layer just below the surface, then finally converges to a bulk value. For example, the interlayer spacing between the surface and subsurface layers of the Co/Fe(001) 11-ML film was calculated to be reduced by about 6.28% compared to the value of the bulk Fe. On the other hands, \( \Delta d \) of the centered layer is closed to zero. This oscillating trend corresponds to the interlayer behavior of a typical metal films.

Magnetic moment

The charge and spin density are the most basic physical quantities in a first principles study. Table 1 shows the magnetic moments of each atom, which are the result of the spin density calculated by Elk method.

As expected from previous studies of surfaces of magnetic thin films [15,23-25], significant magnetic moments are induced in the Co capping atoms, considering the experimentally observed and calculated magnetic moment of bulk Co is 1.65 and 1.49 \( \mu_B \) respectively. Table I presents the profile of the magnetic moment in a Fe(001) film capped by a Co monolayer, as determined by calculations for slabs of increasing Fe thickness. The Co surface, which is in direct contact to the Fe interface has the magnetic moment of about 1.83 \( \mu_B \), i.e. approximately 10% increased value
compared to the spin moment of bulk Co. Interface Fe(S-1) atoms also exhibit large magnetic moment over 2.3 $\mu_B$, however, in the deeper Fe layers we find long-range oscillatory decaying magnetic moments.

Table 1: Calculated atomic-resolved magnetic moments of Co/Fe(001) with various Fe thickness, from 5-to 11-MLs. (S) and (S-n) denote the surface and the nth layer below the surface.

<table>
<thead>
<tr>
<th>Fe Thickness</th>
<th>Co(S)</th>
<th>Fe(S-1)</th>
<th>Fe(S-2)</th>
<th>Fe(S-3)</th>
<th>Fe(S-4)</th>
<th>Fe(S-5)</th>
<th>Fe(S-6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-MLs</td>
<td>1.826</td>
<td>2.307</td>
<td>2.068</td>
<td>1.988</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7-MLs</td>
<td>1.833</td>
<td>2.319</td>
<td>2.057</td>
<td>1.999</td>
<td>2.062</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9-MLs</td>
<td>1.836</td>
<td>2.329</td>
<td>2.084</td>
<td>2.037</td>
<td>2.064</td>
<td>2.017</td>
<td></td>
</tr>
<tr>
<td>11-MLs</td>
<td>1.834</td>
<td>2.325</td>
<td>2.073</td>
<td>2.03</td>
<td>2.07</td>
<td>2.044</td>
<td>2.051</td>
</tr>
</tbody>
</table>

**Magnetocrystalline anisotropy**

The MCA energy is defined as the total energy difference between in-plane and perpendicular magnetizations to the film surface. According to perturbation theory [26], the MCA energy is due to spin-orbit coupling and defined as

$$E_{\text{MCA}} \approx \sum_{\sigma} \left( \langle \sigma | L_z | u \rangle \langle \sigma | L_z | u \rangle \right) - \left( \langle \sigma | L_z | u \rangle \langle \sigma | L_z | u \rangle \right)$$

(1)

Where $\xi$ is the spin-orbit coupling constant. $\sigma(u)$ and $\sigma(e_{\text{up}})$ represent eigenstate and eigenvalue of occupied (unoccupied) state, respectively.

As the denominator $e_{\sigma} - e_{\sigma^\prime}$ becomes smaller, the MCA energy becomes stronger. Therefore, the states near the Fermi energy level play an important role in determining the MCA energy. As can be seen from equation (1), the $<\sigma|L_z|u>$ term contributes to the perpendicular MCA while the $<\sigma|L_z|u>$ term contributes to the in-plane MCA energy. Therefore, if the orbital magnetic quantum number of the $\sigma$ state is equal to the that of the $u$ state, they lead to the perpendicular MCA. However, a difference of 1 in the orbital magnetic quantum number between the $\sigma$ and $u$ states lead to the in-plane MCA. As a result, the perpendicular MCA is affected by $<\sigma|L_z|x^2-y^2>$ and $<\sigma|L_z|yz>$ couplings, and the in-plane MCA can be expressed via $<\sigma|L_z|xz,yz>$ and $<\sigma|L_z|x^2-y^2,xy>$ couplings.

Figure 3 presents the calculated MCA energies of the Co/Fe(001) film as a function of the Fe thickness. The 5-MLs Fe(001) film capped by Co exhibits the lowest MCA energy of $\sim 0.10$ meV. However, it increases monotonically with the Fe thickness, and reaches to $\sim 0.50$ meV at 9-MLs Fe(001) covered by Co surface. After the MCA energy of Co/Fe(001) film shows a maximum value of about 0.50 meV at 9-MLs Fe(001), it is saturated to around to about 0.40 meV, as shown in Figure 3. The MCA energy behavior with respect to the Fe thickness indicates that the enhancement of the MCA energy comes purely from surface and interface effects. To investigate how the capping of a Co monolayer changes the electronic structure of the Fe(001) film and also why the values of MCA energy of 5-MLs and 9-MLs Co/Fe(001) are so different, we present density of states (DOS) of Co(S) and Fe(S-1) of 5-MLs and 9-MLs Co/Fe(001) films in Figure 4 and Figure 5.

**Electronic structures**

A single electron energy spectrum is analyzed to understand the magnetism and magnetic anisotropy of Co/Fe(001) film microscopically. Figure 4 and Figure 5 show the $e_g(x^2-y^2)$ and $t_{2g}$ (xy, xz(yz)) states of Co(S) and Fe(S-1), which play a major role in determining the magnetic anisotropy of Co/Fe(001) films for the Fe thickness of 5-MLs (MCA energy : 0.110 meV) and 9-MLs (MCA energy : 0.475 meV), respectively. The majority spin states are almost filled for both Co(S) and Fe(S-1). Especially, this tendency is much clearly shown in the $e_g$ state. Therefore, the role of the
majority spin states on magnetism, including magnetic anisotropy, is relatively limited. The DOS of minority spin states shows a complex shape compared to that of majority spin states, especially near the Fermi level.

Figure 4: Partial density of states of Co(S) and Fe(S-1) of Co/Fe(001) film with 5-MLs Fe capped by Co surface.

Figure 5: Partial density of states of Co(S) and Fe(S-1) of Co/Fe(001) film with 9-MLs Fe capped by Co surface.
Compared with the DOS of the CoFe system from Ref. [27,28,14], which showed the strong perpendicular MCA, the x²-y² and xy states which because perpendicular MCA are placed close to the Fermi level in present Co/Fe(001) film systems. However, for 5-MLs Fe(001) film with Co capping (Figure 4), the z² state in Co(S) is also closer to the Fermi level than that of 9-MLs Fe(001) film with Co capping (Figure 5). As can be seen from equation (1), the z² state contributes only to the in-plane MCA. Furthermore, as shown in Figure 2, the surface interlayer distance of Co(5-MLs)-Fe(5-MLs) film is relatively narrow compared to that of 9-MLs Fe(001) film. As a result, the width of the z² band becomes wider, while the x²-y² and xy bands become narrower and higher. Therefore, Co capped Fe(001) 5-MLs film exhibit lower MCA energy, while the perpendicular MCA of 9-MLs Fe(001) film with Co surface reaches ~0.5 meV.

Conclusion
In this study, the magnetism and magneto crystalline anisotropy of Co/Fe(001) film were calculated and analyzed by a first principle calculation method using VASP and Elk. When the in-plane lattice constant \( a = 2.796\text{Å} \), the magnetic moments of Co and Fe were increased to over \(-1.8\) and \(2.3\) \(\mu_B\) at the surface and the interface, respectively. Co/Fe(001) film was found to have perpendicular MCA regardless of the Fe thickness. Especially, the perpendicular MCA of 9-MLs Fe(001) film with Co surface reaches ~0.5 meV. From the analysis of the electronic structures, we found that Co surface and Fe interface layers play a crucial role to determine MCA energy of the system.

Acknowledgement
None.

Conflict of Interest

No conflict of interest.

References
20. The Elk Code.