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Magnetic Anisotropy of Pd/Co/Pd Ultrathin Film: Interface Vacancy Defect and O Diffusion Effect

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Using first principles calculation, we investigated the magnetic anisotropy of Pd/Co/Pd ultrathin film. Here, we explored the magnetic anisotropy of pristine Pd/Co/Pd ultrathin film and also interface vacancy defect (Pd or Co) and the oxygen diffusion as well. No substantial change in the magnetic moment is found in the vacancy defect and also in the O diffusion structure relative to the pristine system. We found that the pristine Pd/Co/Pd system has a perpendicular magnetic anisotropy of 1.37 meV/cell. This perpendicular magnetic anisotropy decreased to 0.46 meV/cell in Pd vacancy defect and it became 0.56 meV/cell in Co vacancy defect. We also obtained similar magnetic anisotropy energy of 0.52 meV/cell in the O impurity system. Although the vacancy defect and O impurity system exhibited a similar magnetic anisotropy, we found that this feature originated from different spin-orbit coupling effect which is sensitive to the sample preparation condition.

Keywords : Pd/Co/Pd ultrathin film, vacancy defects, impurity defects, magnetic anisotropy

1. Introduction

In the last few decades, magnetocrystalline anisotropy of low dimensional magnetic material has received tremendous research interest because it is one of the most important physical properties found in magnetic materials and also for potential device applications. Indeed, the magnetic anisotropy can be changed from in-plane to perpendicular or vice versa due to several factors; film thickness, impurity effect, defect, or capping. This is the so-called spin reorientation transition. This feature is found in numerous low dimensional magnetic systems, and it brings many intriguing fundamental issues in magnetism. However, for device applications, the perpendicular magnetic anisotropy is closely related to many novel potential applications [1, 2] such as quantum information procession, storage [3, 4], and magnetic information hard disks because a high enough perpendicular is required to overcome thermal spin fluctuation.

Regarding the perpendicular magnetic anisotropy, the most well-known high perpendicular magnetic anisotropy systems are FePt and CoPt alloys, and also such a huge perpendicular magnetic anisotropy is found in ferromagnetic/non-magnetic multilayer structures. For instance, FeCo/Pd multilayer shows perpendicular magnetic anisotropy when the film thickness is in the range of 4-14 monolayers. The B2 type Fe/Co alloy film also displays spin reorientation from perpendicular to in-plane magnetization when the film thickness reaches roughly 15 monolayers owing to a tetragonal distortion [5]. Along with these multilayer systems, the Pd/Co multilayer system also has been extensively investigated because of its high perpendicular magnetic anisotropy and large saturation magnetization [6]. It has been reported that the perpendicular magnetic anisotropy is preserved if the Co to Pd ratio is less than or equal to 1 and the thickness of Co layers is not more than 5 Å [7]. Besides, the perpendicular magnetic anisotropy is dependent on the Co layer thickness [8]. All these features indicate that the magnetic anisotropy of thin film or multilayer structure is strongly affected by the geometry of the sample even in very clean conditions. However, in realistic sample preparation conditions, the sample may have an imperfect crystal structure. For instance, vacancy defects or impurities may exist in a targeting sample. Thus, in this report, we will consider the Pd/Co/Pd ultrathin film and investigate the influence of Pd and Co interface vacancy defect, and also the oxygen impurity effect on the magnetic anisotropy of the Pd/Co/Pd ultrathin film.

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2. Computational Method

We employ the projector augmented wave (PAW) method [9, 10] as implemented in the Vienna Ab-initio Simulation Package (VASP) [9, 11] with a plane wave basis energy cutoff of 500 eV for the full geometry optimization. We consider the generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) [12] exchange-correlation functional with a total energy convergence criterion of 10^{-6} eV and the Hellman-Feynman force convergence of 0.01 eV/Å for the optimized atomic position relaxation. The vacuum space in the z-direction is set to 15 Å to avoid an artificial interaction with a neighboring unit cell. A supercell size of 2 × 2 × 1 is considered for Pd/Co/Pd ultrathin film with the O impurity, Pd, or Co vacancy defect system. The magnetic anisotropy energy (MAE) is calculated by calculating the total energy difference between the in-plane (E_{100}) and the out-of-plane (E_{001}) MAE directions: (MAE = E_{100} – E_{001}) using a grid of 11 × 11 × 1 k-mesh in the first Brillouin zone.

3. Results and Discussion

In the Pd/Co/Pd ultrathin film system, both Pd and Co films are extracted from the Pd and Co bulk structures in (111) direction [13, 14]. Here, we consider 5 layers of Co and 6 layers of Pd thickness (3 on top and 3 on bottom). Fig. 1 shows the schematic illustration of the Pd/Co/Pd ultrathin film system. We performed full structure relaxation and obtained the lattice parameters of a = b = 2.692 Å. The thickness of the Co layer is 7.653 Å while that of the Pd layer is 4.765 Å, and the interlayer distance between the Pd and Co layers is around 2.115 Å. We calculated the magnetic moment of the Pd/Co/Pd system and obtained the total magnetic moment of 10.15 μ_B per unit cell. The Co atom at the central layer has a magnetic moment of 1.71 μ_B while the interface Co atom has a magnetic moment of 1.85 μ_B due to the hybridization with the Pd atom. Consequently, the interface Pd atom has an induced magnetic moment of 0.33 μ_B. We also explored the spin-orbit coupling (SOC) induced magneto-crystalline anisotropy energy (MAE). The pristine Pd/Co/Pd ultrathin film structure has an out-of-plane magnetic anisotropy of 1.37 meV/cell, and this is close to the previously reported value of the multilayer structure [15].

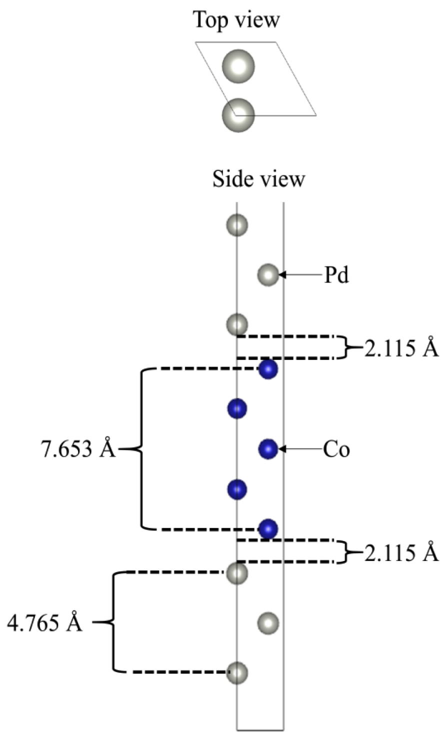

Fig. 1. (Color online) Schematic illustration of (a) the pristine ultrathin Pd/Co/Pd film structure with side and top of views.

We now focus on the central issue of this report. Here, we consider the Pd and Co interface vacancy defects and also O impurity diffusion into the Pd/Co/Pd ultrathin film structure. So, we explored three types of effects; i) Pd interface vacancy defect ii) Co interface vacancy defect iii) O impurity diffusion into the Pd/Co/Pd thin film. First, we present the Pd or Co vacancy defect at the interface, and Fig. 2(a)-(b) shows the schematic illustration. Here, we used 2 × 2 × 1 supercell, and this corresponds to 4.5 % vacancy defect concentration. After structure relaxation, we found no substantial change in the interlayer distance between Co and Pd layers because the calculated interface distance is 2.114 Å in both Pd and Co vacancy defect structures. On the other hand, we also studied the effect of the O diffusion into the Pd/Co/Pd system and the schematic illustration of the 2 × 2 supercell is presented in Fig. 2(c). Here, we initially put the O impurity at the middle of the Pd and Co interface (red circle). However, after structure relaxation, the O impurity is diffused into the Co layers (red circle). Nonetheless, we obtained that the interlayer distance between Co and Pd layers is almost unchanged. Besides, we found no substantial change in the magnetic moments of Pd and Co atoms in Pd and Co vacancies defect systems, and also in the O impurity defect system compared with those in the pristine Pd/Co/Pd ultrathin film system. It is worth noting that the magnetic moment itself is independent of the orbital character because only the number of occupied electrons in each spin band is related to the magnetic moment. However, the magnitude of the magnetic anisotropy and magnetization direction can be strongly

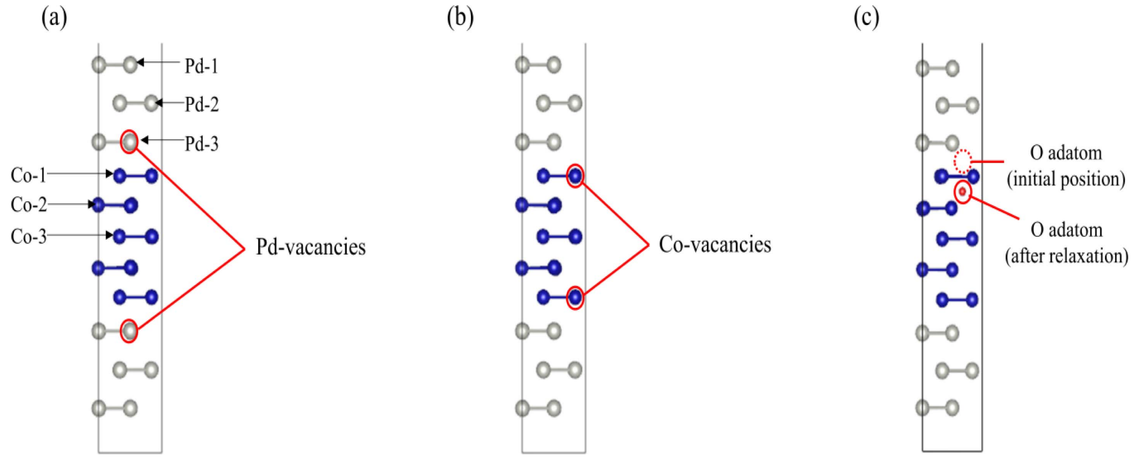

Fig. 2. (Color online) Schematic illustration of the side view of 2 × 2 × 1 ultrathin Pd/Co/Pd film structure with (a) interface Pd vacancy defect (b) interface Co vacancy defect, and (c) O impurity defect.

dependent on the orbital feature owing to the SOC effect. Thus, we expect that the magnetic anisotropy will change although the magnetic moment remains almost intact in the vacancy or impurity system. To explore this, we calculated the magnetic anisotropy in vacancy and impurity systems. We found that the interface Pd vacancy defect system still has perpendicular magnetic anisotropy, but the magnetic anisotropy energy is decreased to 0.46 meV/unit cell from 1.37 meV/cell in pristine structure. The Co interface vacancy defect system also has a perpendicular magnetic anisotropy of 0.56 meV/unit cell. We also found a similar magnitude of magnetic anisotropy of 0.52 meV/unit cell in the O impurity system. Overall, we found that the perpendicular magnetic anisotropy is substantially suppressed in the vacancy defect and O impurity system compared with that found in the pristine Pd/Co/Pd ultrathin film.

Indeed, we expected that each system (Pd and Co vacancy, and also O impurity) would display different magnetic anisotropy, but it turned out that all the systems displayed similar behavior. To reveal the origin of this feature, we calculated the contribution to the magnetic anisotropy from each layer. Fig. 3 shows the calculated results. Due to the symmetry, we only present the first three Co and Pd layers. Here, we sum all the contributions from each atom and divide them by the total number of atoms in a given layer. So, we present the average contribution per atom in each layer. In the pristine system, all the Co atoms contributed to the perpendicular anisotropy, and their contributions are almost the same while the contribution from the Pd layer is site dependent. For instance, the interface Pd had no contribution whereas the other two layers have almost the same magnitude with the opposite contribution. As shown, the surface Pd layer (Pd-1) has an in-plane contribution whereas the subsurface Pd layer (Pd-2) shows a perpendicular anisotropy. In contrast, the interface Pd layer (Pd-3) has no contribution. Consequently, the net contribution from entire Pd atoms is negligible. So, we conclude that the perpendicular magnetic anisotropy in pristine Pd/Co/Pd thin film is originated from Co layers. In the Pd interface vacancy defect system, the Co atoms still maintained perpendicular magnetic anisotropy, but the perpendicular contribution is slightly suppressed. Particularly, the suppression at the interface Co layer (Co-1) is noticeable among all other Co layers. We also found a substantial change in the interface Pd layer because a large in-plane contribution appeared. Meantime, the in-plane perpendicular contribution from the surface and subsurface Pd layers is reduced. This is

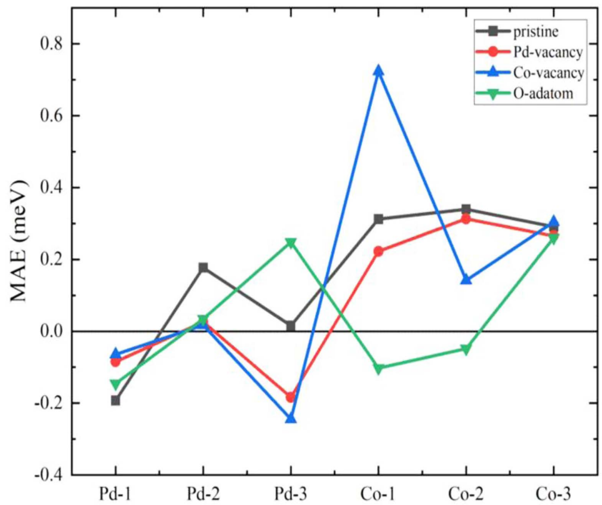

Fig. 3. (Color online) Layer dependent planar averaged contribution to the magnetic anisotropy. Here we present the first three Co and Pd layers owing to the symmetry.

the reason why the perpendicular magnetic anisotropy of the Pd vacancy defect system is almost half of the pristine system. In the interface Co vacancy defect system, the contributions from the Pd layers are almost the same as those found in the Pd vacancy defect system. However, we found a substantial change in the role of Co layers. For instance, we found a large enhanced perpendicular anisotropy from the interface Co layer, but the perpendicular contribution from the Co layer next to the interface layer is largely suppressed (Co-2 layer). Due to these changes in the Co layer, no dramatic change in the final magnetic anisotropy is obtained. In the O impurity system, as mentioned above, the total magnetic anisotropy is unchanged compared with those found in the Pd and Co interface vacancy defect systems. Nonetheless, we found substantial changes in the contribution of both Co and Pd layers. Unlike the previous systems, two Co layers (Co-1 and Co-2) have in-plane contributions due to the hybridization with the O impurity atom. In contrast, the interface Pd layer has a perpendicular contribution. Consequently, the net perpendicular magnetic anisotropy is almost unchanged. Overall, we found that the magnetic anisotropy either vacancy defect or O impurity system has more or less the same magnetic anisotropy, but the origin is quite different from each other.

As remarked above, the magnetic anisotropy is strongly sensitive to the orbital characters in both unoccupied and occupied states near the Fermi level through spin-orbit coupling (SOC). So, we further analyze the change in the magnetic anisotropy affected by interface vacancy defect and O impurity. The analysis can be conducted based on the following expression

$$\mathrm{MAE} = \xi^2 \sum_{u,o,\alpha,\beta}(2\xi_{\alpha\beta} - 1)\left[\frac{|\langle u,\alpha|\widehat{L_z}|o,\beta\rangle|^2 - |\langle u,\alpha|\widehat{L_x}|o,\beta\rangle|^2}{\varepsilon_{u,\alpha} - \varepsilon_{o,\beta}}\right] \quad (1)$$

where ξ is the strength of SOC and $\varepsilon_{u,\alpha}$ and $\varepsilon_{o,\beta}$ are the energy levels of unoccupied and occupied states with spin α and β. As an illustration, we considered interface Pd and Co layer because these two layers are most sensitive to their environment. Fig. 4 shows the SOC elements for the interface Co atom while Fig. 5 shows the interface Pd atom. The positive value means perpendicular magnetic anisotropy while the negative value represents the in-plane contribution. As shown in Fig. 4, the largest contribution to the perpendicular magnetic anisotropy originated from the SOC between $d_{x2\text{-}y2}$ - d_{xy} orbitals, and another perpendicular anisotropy appeared from d_{xz} - d_{yz} SOC while an in-plane contribution appeared from the SOC between d_{z2} - d_{yz}. This feature is generally preserved in the pristine, Pd, and Co interface vacancy defect systems although the magnitude is slightly changed. However, we

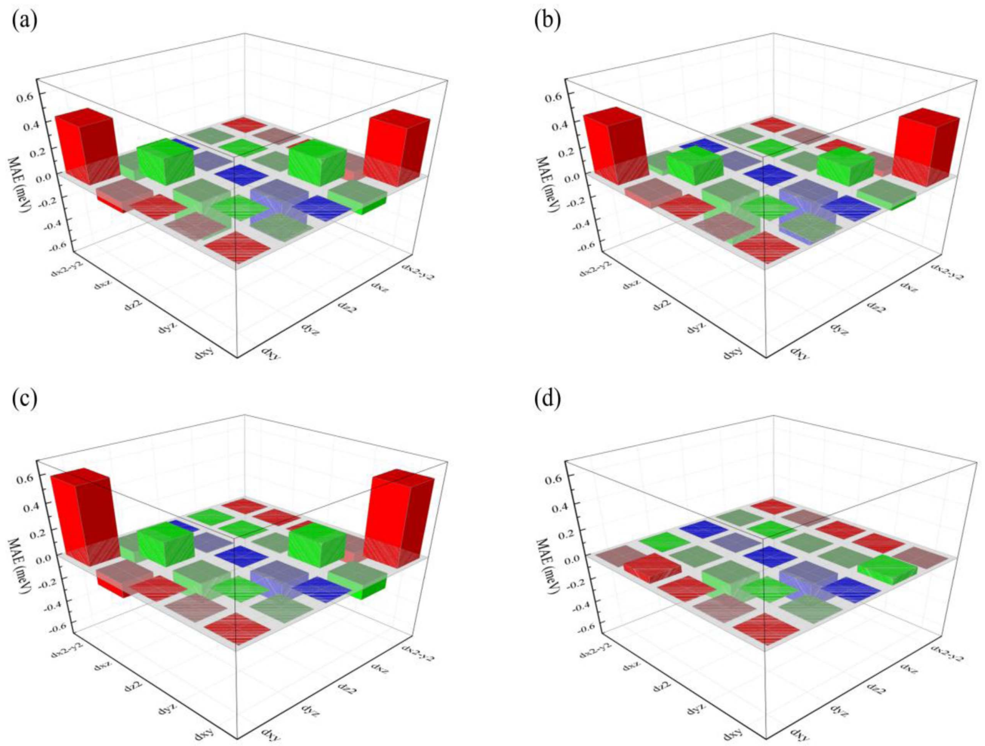

Fig. 4. (Color online) SOC resolved MAE of the interface Co atom in (a) the pristine ultrathin Pd/Co/Pd film, (b) Pd vacancy defect, (c) Co vacancy defect, and (d) O impurity defect.

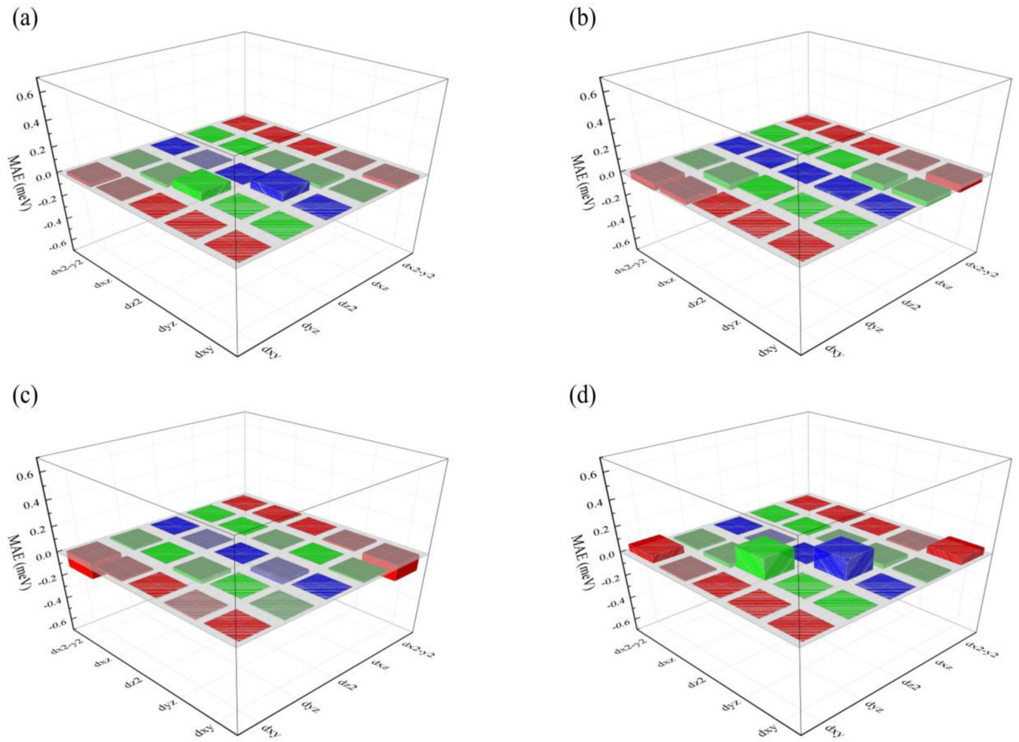

Fig. 5. (Color online) SOC resolved MAE of the interface Pd atom in (a) the pristine ultrathin Pd/Co/Pd film, (b) Pd vacancy defect, (c) Co vacancy defect, and (d) O impurity defect.

found a substantial change in the O impurity system. The contribution to the magnetic anisotropy from d_{x2-y2} - d_{xy} SOC almost vanished while the in-plane contribution from d_{z2} - d_{yz} SOC is still maintained. On the other hand, the SOC contribution of the interface Pd atom also exhibited a different behavior as shown in Fig. 5. In the pristine systems, the interface Pd layer has small perpendicular anisotropy from d_{z2} - d_{yz} SOC orbitals while a small in-plane contribution is found from d_{x2-y2} - d_{xy}. Then, the net effect from the interface Pd layer is almost negligible. However, in both Pd and Co interface vacancy defect systems, the perpendicular contribution from d_{z2} - d_{yz} SOC almost vanished, and the in-plane contribution from the d_{x2-y2} - d_{xy} SOC is further enhanced. In the O impurity system, we observed substantial change. For instance, d_{x2-y2} - d_{xy} SOC has an in-plane contribution in the vacancy defect system, but it shows a perpendicular anisotropy. Furthermore, we also obtained a large perpendicular anisotropy from d_{z2} - d_{yz}. This resulted in a large perpendicular anisotropy from the interface Pd layer. Overall, it seems that the net magnetic anisotropy is insensitive to the existence of interface Pd, Co, vacancy defect, and also O impurity effect. Nonetheless, we find that this feature originated from different behavior in the SOC matrix element.

4. Conclusion

In summary, we investigated the vacancy and impurity induced magnetic anisotropy of the ultrathin Pd/Co/Pd film. We considered both interface Pd, Co vacancy defect, and also O impurity effect. The pristine system has a total magnetic moment of 10.61 μ_B per unit cell and no substantial change is found in the magnetic moments of the Pd, Co interface vacancy defect, and also O impurity systems. We found that the pristine Pd/Co/Pd thin film has a perpendicular magnetic anisotropy of 1.37 meV/cell, and the perpendicular magnetic anisotropy is decreased by more than half in the interface Pd and Co vacancy defect systems and also in the O impurity structure. Seemingly, the net magnetic anisotropy is almost insensitive to the interface vacancy or O impurity defect. However, through the SOC matrix analysis, we found that the SOC itself is strongly sensitive to the sample environment and each layer contributed to the magnetic anisotropy differently.

Acknowledgments

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