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Abstract. First-principles calculations of the magnetic anisotropy energies of Pd/Co(111) and Pd/Co(001) metallic multilayers have been performed to investigate the orientational dependence of the magnetic anisotropy. The calculated results indicate perpendicular magnetic anisotropy for both systems in accordance with experiments, and the anisotropy energy of the (111) oriented multilayer is more than four times larger than that of the (001) multilayer. The perpendicular magnetic anisotropies of these systems are explained by the same electronic origin, a large LDOS of $|m| = 2$ character of Co minority spin near the Fermi energy. The small anisotropy of the (001) multilayer can be attributed to the weaker hybridization at the interface as compared to the case of the (111) system.

1. Introduction

In recent years, the presence of perpendicular magnetic anisotropy in metallic multilayers has attracted a great deal of interest because of the possible technological advances in magnetic and magneto-optical recording [1–5]. Metallic multilayers, such as Pt/Co, Pd/Co and Au/Co, exhibit large positive uniaxial anisotropies when the magnetic layer thickness is reduced to a few monolayers. In spite of many experimental and theoretical studies related to the understanding of magnetic anisotropy, the origin of perpendicular anisotropy in multilayered magnetic thin films remains an important question [2–17].

It has been established phenomenologically that perpendicular anisotropy is associated with the interfaces between different metals, since the effective uniaxial anisotropy energy K_u can be expressed as follows as a function of magnetic layer thickness t:

$$K_u = K_v + 2K_s/t. \tag{1}$$

Here, K_v and K_s represent a volume and an interface contribution to the magnetic anisotropy, respectively. K_v contains contributions from shape, magnetocrystalline and magneto-elastic anisotropy, while K_s is interpreted as interface anisotropy, which results from the broken symmetry of interface atoms, Néel's surface anisotropy [18]. Equation (1) holds in most of the experiments at least when the magnetic layer is sufficiently thick that the value of K_v, which includes the magneto-elastic anisotropy, can be assumed to be constant irrespective of the magnetic layer thickness. There are several other factors, such as strain, roughness, atomic mixing at interfaces and crystal orientation, which can strongly influence the interface anisotropy.

Previous evidence for an orientational dependence of the magnetic anisotropy in metallic multilayers has been reported for Pd/Co [4] [19], Pt/Co [20], Cu/Co [21] and Cu/Fe [21]. In the case of Pd/Co [4], large differences were observed between (111) textured polycrystalline films deposited on glass and (001) epitaxial superlattices evaporated on NaCl. Decreasing the Co layer thickness, den Broeder *et al* found crossover from in-plane to perpendicular behaviour for the (001) samples between one and two atomic layers. This is in marked contrast to the case for their (111) textured films, which became perpendicular at six atomic layers. The MBE growth of several Pt/Co multilayers along the [001], [110] and [111] directions was also reported [20]. Large variations in the hysteresis loop behaviour indicated an easy plane for the (001) sample and a perpendicular easy axis for the (111) and (110) multilayers.

On the other hand, Engel *et al* [19] have studied the uniaxial magnetic anisotropy of Pd/Co grown under identical conditions by MBE along three crystal axes: [001], [110] and [111]. Their measurements demonstrate that the large systematic variations of the anisotropy energy with crystal orientation result solely from differences in the volume contribution to the anisotropy, and the perpendicular interface anisotropy is independent of the epitaxial orientation. Recently Kief and Egelhoff [21] have studied the perpendicular magnetic anisotropy of Fe and Co on Cu(001), Cu(110) and Cu(111). Their results also suggest a common magnetic interface anisotropy energy independent of crystal orientation.

We have therefore undertaken a study of an orientational dependence of the uniaxial anisotropy in Pd/Co metallic multilayers. In order to clarify the dependence of magnetic anisotropy on crystal orientations, we have calculated the magnetic anisotropy energies of (001) and (111) oriented metallic multilayers from first principles by means of the linear muffin-tin orbital method within the atomic spheres approximation.

2. Method of calculation

The calculation of the electronic structure has been done from first principles using the linear muffin-tin orbital method within the local spin-density approximation [22]. The magnetocrystalline anisotropy energy ΔE, which is the difference of the total energies for perpendicular ([001]) and in-plane ([100]) orientation of the magnetization, is given by the difference of sums over Kohn–Sham eigenvalues:

$$\Delta E = \sum_{i,k}^{occ} \varepsilon_i([100], \boldsymbol{k}) - \sum_{i,k}^{occ} \varepsilon_i([001], \boldsymbol{k}). \tag{2}$$

Here $\varepsilon_i([001], \boldsymbol{k})$ and $\varepsilon_i([100], \boldsymbol{k})$ are the Kohn–Sham eigenvalues calculated with [001] and [100] spin polarization, respectively. The calculation has been described in detail in our previous papers [16, 17].

We have calculated the anisotropy energies for two different crystal orientations, (111) and (001), of Pd/Co multilayers. One period of a (111) oriented multilayer consists of two monolayers of Pd and one monolayer of Co. The stacking sequence of the monolayer is chosen to be ABCABC like that of the close-packed planes of an fcc structure. As for the (001) oriented multilayer, a period consists of three monolayers of Pd and one monolayer of Co.

Since, in the results of Engel *et al* [19], equation (1) holds very well for a wide range of t_{Co} including the multilayer with the smallest t_{Co}, it seems that an estimate of orientational effects from the multilayer with one monolayer of Co in a period in this study will not be an overestimate. As for the result of den Broeder *et al* [4], the value of $K_u t_{Co}$ for the (111) orientation is smaller than that calculated from equation (1) when t_{Co} is small. As a

consequence the estimation of K_s of (111) orientation from the multilayer which contains one monolayer of Co in a period might underestimate the orientation effect.

In both systems, the interface is coherent and the value of the interatomic distance in the in-plane direction is taken to be equal to the bulk value of Pd (a), since experimentally in most cases, the thickness of the Pd layer is greater than that of the Co layer. The interplanar distance of Pd (d_{Pd-Pd}) is taken to be equal to the bulk value. On the other hand, the interplanar distance between the Pd layer and the Co layer (d_{Co-Pd}) is assumed to be equal to the average of the bulk values of Pd and Co. We have verified that our calculations are not sensitive to changes in structure parameters of a few per cent. The structure parameters (a, d_{Co-Pd}, d_{Pd-Pd}) and atomic sphere radii (R_{Co}, R_{Pd}) adopted in the calculations are summarized in table 1.

Table 1. Structure parameters used in the calculations and the results for magnetic anisotropy energy.

	a (Å)	d_{Co-Pd} (Å)	d_{Pd-Pd} (Å)	R_{Co} (Å)	R_{Pd} (Å)	ΔE (meV/unit cell)
Pd(2 ML)/Co(1 ML)(111)	2.7505	2.1465	2.2458	1.4107	1.5480	1.12
Pd(3 ML)/Co(1 ML)(001)	2.7505	1.8586	1.9449	1.4040	1.5407	0.24

3. Results and discussion

The results for the calculated anisotropy energies, ΔE, are also shown in table 1. All of the calculations were done with 9216 and 12 288 k-points in the whole Brillouin zone for Pd/Co(111) and Pd/Co(001) oriented multilayers, respectively. These numbers of k-points are sufficient to achieve a convergence better than 0.1 meV/unit cell. When ΔE is positive, the system shows a perpendicular anisotropy. It can be seen that the anisotropy energies are positive for both orientations in accordance with experiments and that the value for the (111) orientation is more than four times larger than that for the (001) orientation. If we use the experimental K_v-values [19], K_s can be calculated from the values in table 1 as 1.42 erg cm^{-2} and 0.65 erg cm^{-2} for (111) and (001) oriented multilayers, respectively.

As mentioned earlier, den Broeder *et al* [4] measured values of K_s for the (111) orientation as 0.92 erg cm^{-2}, whereas the highest value observed for K_s in the (001) orientation was found to be only 0.32 erg cm^{-2}. The fact that the calculated anisotropy energy of the (111) oriented multilayer is larger than that of the (001) multilayer is in agreement with their experiment. The experimental values are, however, somewhat smaller than the calculated values. Purcell *et al* [23] performed RHEED and LEED studies of Co films formed on a Pd(111) single-crystal substrate. They found that Co grows epitaxially, incoherently and relatively flat in the (111) orientation right from the initial stage of growth. It was shown by RHEED measurements that the interplanar distances of Co layers immediately relax to values close to their bulk interplanar distance. However, extra diffraction LEED patterns were observed around the main Co spots which suggests that the Co lattice is periodically modulated owing to incoherent epitaxy on Pd(111). In our study of the strain dependence of the magnetic anisotropy of Pd/Co multilayers [24], it was found that decreasing the interatomic distance of Co in the in-plane direction results in a reduction of perpendicular anisotropy energy. Therefore the discrepancy between the experimental and our theoretical values could be attributed to the difference between the experimentally observed incoherent structure and the perfectly coherent structure in our calculations.

On the other hand, Engel *et al* [19] have carried out structural and magnetic studies of Pd/Co multilayers in all three low-index orientations (001), (011) and (111). The surface anisotropies in all orientations were found to be identical, $K_s = 0.63$ erg cm^{-2}. As for the (001) orientation, our theoretical value is remarkably close to their experimental value. Also in this case, the discrepancy for the (111) orientation could be attributed to the difference between the experimentally observed incoherent structure and the perfectly coherent structure in our calculations.
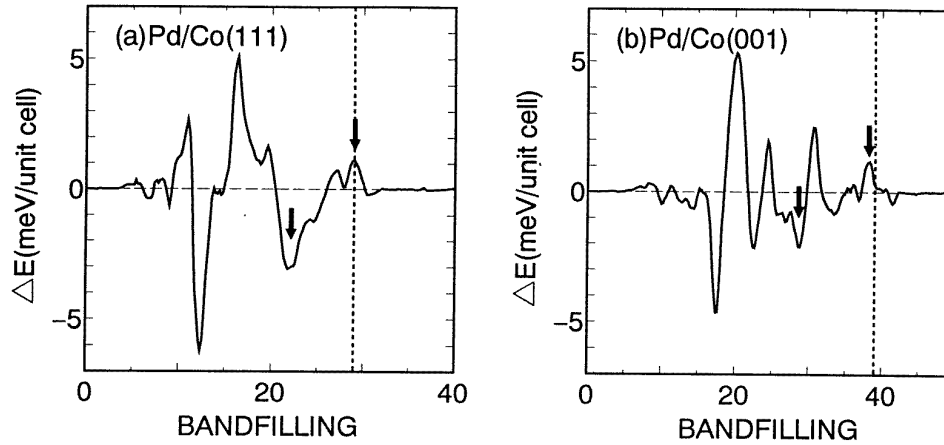
Figure 1. The dependence of the anisotropy energies of Pd/Co multilayers as a function of band-filling. The band-filling is the number of valence electrons in the unit cell. The numbers of valence electrons in the unit cell are 29 and 39 for (111) and (001) oriented multilayers, respectively. These are indicated by vertical dotted lines. (a) Pd(2 ML)/Co(1 ML)(111) (here the positions of the arrows correspond to band-fillings of 22 and 29). (b) Pd(3 ML)/ Co(1 ML)(001) (here the positions of the arrows correspond to band-fillings of 29 and 38).

We have also calculated the anisotropy energy as a function of band-filling. Here, band-filling represents the number of valence electrons per unit cell. The results are shown in figure 1. In both cases the anisotropy energy shows an oscillatory behaviour. In the case of a (111) oriented multilayer, there exists a peak near the Fermi level. The Fermi level comes near the top of this peak and consequently this system exhibits a large perpendicular anisotropy. A peak of almost the same height can also be seen near the Fermi level in the case of a (001) oriented multilayer, but the Fermi level comes at the right-hand side of the peak and results in a small perpendicular anisotropy. If the band-filling is smaller, and thus the Fermi level comes right at the top of the peak, the anisotropy energy of the (001) oriented multilayer will not be so different from that of the (111) oriented multilayer.

The magnetic anisotropy originates from the spin–orbit interaction, which couples eigenstates ψ_{nk} and $\psi_{n'k}$ with eigenvalues ϵ_{nk} below the Fermi energy (ϵ_F) and $\epsilon_{n'k}$ above ϵ_F. Here, n (n') and k label the energy band and a point in the Brillouin zone, respectively. If the level splitting $\epsilon_{nk} - \epsilon_{n'k}$ is much larger than the spin–orbit coupling parameter ξ, perturbation theory can be used to calculate the anisotropy energy. The corrections to the energy level ϵ_{nk} due to the spin–orbit coupling are given as follows:

$$\Delta\epsilon_{nk} = \sum_{(\epsilon_{n'k} > \epsilon_F)}^{n'} \frac{|\langle\psi_{nk}|H_{S.O.}(\theta, \varphi)|\psi_{n'k}\rangle|^2}{\epsilon_{nk} - \epsilon_{n'k}}. \tag{3}$$

The expression is given within the lowest order, i.e., second order, because the diagonal matrix elements of $H_{S.O.}(\theta, \varphi)$ are zero. Here, $H_{S.O.}(\theta, \varphi)$ is a spin–orbit coupling matrix, $\xi \boldsymbol{l} \cdot \boldsymbol{s}$, and the magnetization is oriented along θ, φ. θ and φ are polar coordinates with respect to a rectangular coordinate system. The z-axis of the coordinate system is chosen normal to the film plane and the x-axis is chosen along a nearest-neighbour direction.

From equation (3), the magnetic anisotropy can be expressed as follows:

$$\Delta E = \sum^{k} \sum_{(\epsilon_{nk}<\epsilon_F)}^{n} \sum_{(\epsilon_{n'k}>\epsilon_F)}^{n'} \frac{\{|\langle\psi_{nk}|H_{S.O.}(\pi/2, 0)|\psi_{n'k}\rangle|^2 - |\langle\psi_{nk}|H_{S.O.}(0, 0)|\psi_{n'k}\rangle|^2\}}{\epsilon_{nk} - \epsilon_{n'k}}.$$

(4)

The negative and positive values of the element

$$\{|\langle\psi_{nk}|H_{S.O.}(\pi/2, 0)|\psi_{n'k}\rangle|^2 - |\langle\psi_{nk}|H_{S.O.}(0, 0)|\psi_{n'k}\rangle|^2\}$$

contribute to perpendicular and in-plane anisotropy, respectively. As for the interaction between the orbitals of the same spin, the matrix elements $\langle d_{x^2-y^2}|H_{S.O.}|d_{yz}\rangle$, $\langle d_{xy}|H_{S.O.}|d_{xz}\rangle$ and $\langle d_{3z^2-r^2}|H_{S.O.}|d_{yz}\rangle$ contribute to the in-plane anisotropy, and the matrix elements $\langle d_{xz}|H_{S.O.}|d_{yz}\rangle$ and $\langle d_{xy}|H_{S.O.}|d_{x^2-y^2}\rangle$ contribute to the perpendicular anisotropy. The relative values of these elements are

$$\langle d_{xz}|H_{S.O.}|d_{yz}\rangle : \langle d_{xy}|H_{S.O.}|d_{x^2-y^2}\rangle : \langle d_{x^2-y^2}|H_{S.O.}|d_{yz}\rangle : \langle d_{xy}|H_{S.O.}|d_{xz}\rangle : \langle d_{3z^2-r^2}|H_{S.O.}|d_{yz}\rangle$$
$$= -1 : -4 : 1 : 1 : 3.$$

These matrix elements exist only for the same k-point. However, since the absolute value of the matrix element $\langle d_{xy}|H_{S.O.}|d_{x^2-y^2}\rangle$ is larger compared to other elements and this element contributes to perpendicular anisotropy via lifting of degeneracy at high-symmetry points in the Brillouin zone, the origin of the perpendicular anisotropy can be discussed qualitatively from the position of the Fermi level relative to the local density of states (LDOS) of $|m| = 2$ character (d_{xy} and $d_{x^2-y^2}$ orbitals) of Co minority-spin d electrons. Here, m is the magnetic quantum number with the quantization axis in the perpendicular direction.

The local densities of states (LDOS) of the (111) and (001) oriented multilayers are shown in figure 2. The electronic states of the majority spin are almost occupied. The hybridization of the electronic states of Co and Pd atoms is larger compared to the case of Ag/Co and Au/Co multilayers reported previously [16]. It can be seen that the LDOS of Co minority spin in the (001) oriented multilayer has large and sharp peaks compared to that of the (111) system. This fact implies a weaker hybridization at the interface in the (001) case. The m-decomposed LDOS of Co is plotted in figure 3. Since the LDOS of Co is rather larger than that of Pd at the Fermi level, only the m-resolved LDOS of Co is considered. As for the (111) oriented multilayer, the increase in the anisotropy energy from the band-filling of 22 to 29, which is indicated by the arrows in figure 1(a), can be attributed to the large LDOS of $|m| = 2$ character of minority spin in the corresponding region, which is also indicated between the arrows, below the Fermi energy (figure 3(a)). Also, in the case of (001) orientation, the anisotropy energy gradually increases from the band-filling of 29 to 38, which is indicated by the arrows in figure 1(b), except for the sharp peak at the band-filling of 31 caused by lifting of degeneracy. This increase can be attributed to the large LDOS of $|m| = 2$ character of minority spin in the corresponding region, which is indicated between the arrows, below the Fermi energy (figure 3(b)). Therefore it is concluded that for both systems, (111) and (001) orientation, the perpendicular magnetic anisotropy is realized by the existence of a large LDOS of $|m| = 2$ character below the Fermi energy.

In the case of (001) orientation, a large LDOS of the $d_{3z^2-r^2}$ orbital, which favours an in-plane anisotropy, exists right at the Fermi level and causes the decrease of ΔE. As
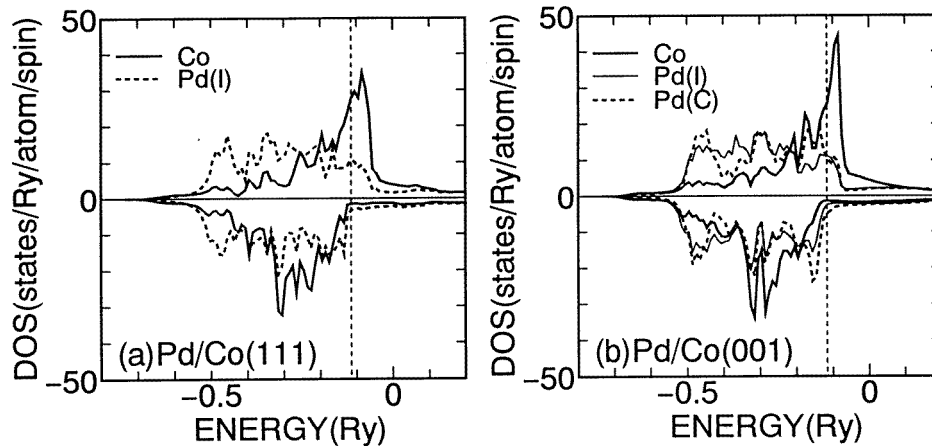
Figure 2. The local density of states (LDOS) of the multilayers. Solid line: the LDOS of Co; thin and dotted lines: the LDOS of Pd. Pd(I) and Pd(C) stand for Pd atoms at the interface and the centre layer, respectively. The Fermi level is indicated by vertical dotted lines. (a) Pd(2 ML)/Co(1 ML)(111). (b) Pd(3 ML)/Co(1 ML)(001).
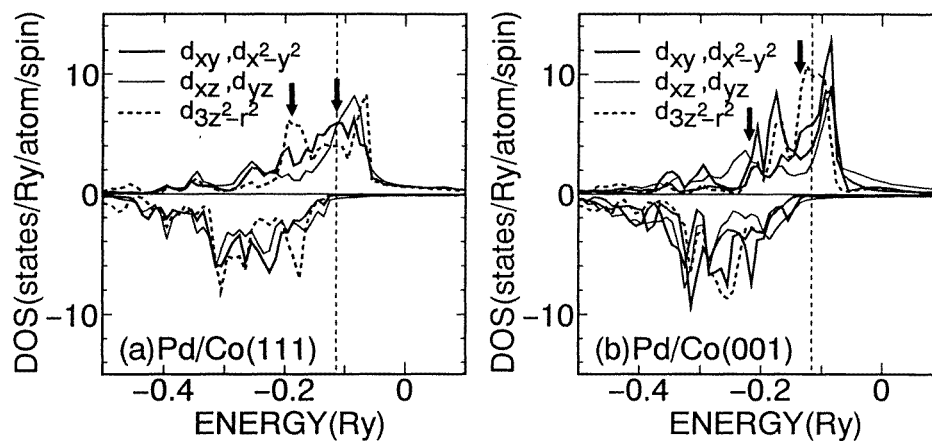
Figure 3. The *m*-decomposed LDOS of Co. Solid, thin and dotted lines correspond to $d_{x^2-y^2}$ (d_{xy}), d_{xz} (d_{yz}) and $d_{3z^2-r^2}$ orbitals, respectively. The Fermi level is indicated by vertical dotted lines. (a) Pd(2 ML)/Co(1 ML)(111) (the positions of the arrows correspond to the band-fillings of 22 and 29). (b) Pd(3 ML)/Co(1 ML)(001) (the positions of the arrows correspond to the band-fillings of 29 and 38).

a consequence, the anisotropy energy ΔE becomes smaller than that of (111) orientation. As reported previously [16], the Ag/Co multilayer is predicted to exhibit a weak in-plane anisotropy in accordance with experiments. The LDOS of Co of the Ag/Co multilayer has relatively large and sharp peaks, which suggests a small hybridization at the interface, and a large LDOS of the $d_{3z^2-r^2}$ orbital exists right at the Fermi level, just as in the case of the Pd/Co(001) multilayer. As mentioned earlier, the hybridization at the interface in a (001) multilayer is smaller than that in a (111) multilayer and consequently the small anisotropy

energy of the (001) system could be explained by the weaker hybridization at the interface compared to the case for the (111) system.

4. Conclusions

The anisotropy energies of (111) and (001) oriented Pd/Co multilayers are calculated from first principles. Both systems show perpendicular anisotropy in good agreement with experiments and the anisotropy energy of the (111) oriented multilayer is more than four times larger than that of the (001) multilayer. The perpendicular magnetic anisotropies of these systems are explained by the same electronic origin, a large LDOS of $|m| = 2$ character of Co minority spin near the Fermi energy. The small anisotropy of the (001) multilayer can be attributed to the weaker hybridization at the interface as compared to the case for the (111) system.

Acknowledgment

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