


## Switching of magnetism via modifying phase shift of quantum-well states by tailoring the interface electronic structure

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We demonstrate control of the magnetism of Pd(100) ultrathin films, which show  $d$ -electron quantum-well-induced ferromagnetism, via modulation of the interface electronic state using density functional calculation. From an analysis based on the phase model, forming the Au/Pd(100) interface induces hybridization of the wave function of  $d$ -electron quantum-well states, and modulates the term of the scattering phase shift as a function of the reciprocal lattice point. In contrast, forming the Al interface, which has only  $s$  electrons at the Fermi energy, cannot modify the scattering phase shift. Our finding indicates the possibility of modifying the phase shift by tailoring the interface electronic states using hybridization of the wave function, and this efficiently changes the density of states near the Fermi energy of Pd films, and the switching between paramagnetism and ferromagnetism occurs based on the condition for ferromagnetism (Stoner criterion).

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### I. INTRODUCTION

For the development of novel electronic devices based on degree of freedom of spin in electrons, the switching of magnetic order using external fields is an idea having the potential to update the concept of current magnetic memory devices [1]. Recently, it was experimentally shown that the magnetism and magnetoanisotropy of Fe, Co, and Pt ultrathin films [2–4] and the proximity-induced magnetism of Pd and Pt ultrathin films could be modulated using electric field [5,6]. The experiment involving x-ray magnetic circular dichroism and first-principles calculations indicated that the microscopic origin of the electric field effect on proximity-induced magnetism in Pt ultrathin films can be explained by a shift of the Fermi level, change in the orbital hybridizations [6,7], and change in the electric quadrupole [8].

In the metal ultrathin film systems used in the electric field effect experiment, however, the electronic states are modified by the size effect and/or the local lattice distortion of metals and the magnetic states are different from those in bulk metals [9–12]. The quantum-well states occurring in ultrathin film formed in metal especially modulate the density of states at the Fermi energy,  $D(\epsilon_F)$ , in an oscillatory manner depending on the film thickness. The period of oscillation in  $D(\epsilon_F)$  is determined by the Fermi wave number of metals [13]. The confined electronic states in the quantum well are described by the phase model [14]

$$2k_z d + \Phi = 2\pi n, \quad (1)$$

where  $k_z$  is the confined wave number,  $d$  is the film thickness,  $\Phi$  is the scattering phase shift at surface and interface, and  $n$  is an integer quantum number. This equation indicates that the

electronic states in the metals are modulated depending on the film thickness. In the standpoint of the Stoner criterion, which is the requirement for the appearance of ferromagnetism in transition metals,

$$ID(\epsilon_F) > 1, \quad (2)$$

where  $I$  is the exchange integral, the modifying of  $D(\epsilon_F)$  may induce the ferromagnetic states of  $3d$  and  $4d$  transition metals. From this mechanism, the magnetoanisotropy of Fe and Co ultrathin films is modulated [15,16]. In addition, we experimentally and theoretically discovered that ferromagnetism appears in Pd(100) ultrathin films in an oscillatory manner depending on the film thickness. This can be explained by the quantum-well states [17–20]. This quantum-well-induced ferromagnetism is modulated by controlling the Fermi level using an electric field [21–23] and changing the quantum-well states using lattice distortion [24–27]. Change in the band dispersion can explain the mechanism by which these control the magnetism.

If the scattering phase shift  $\Phi$  is modulated using an external field, it is believed that the magnetism of the entire film is controlled by modulating only the surface and/or interface electronic states of the films. The  $\Phi$  is just a parameter in the phase model, however, also the current proposed method for controlling  $\Phi$  only involves modifying the work function of materials [28,29]. This is because the interpretation of  $\Phi$  from the standpoint of electronic states is inarticulate. By clarifying the method for controlling  $\Phi$ , it is possible to develop a novel magnetic switching device by which it is possible to control the size effect. This will expand the scientific principle upon which is based magnetic switching by band engineering using quantum-well states [30].

In this paper, we focus on the stacking effect of Au and Al monolayers on the magnetism of Pd(100) ultrathin film. Au has  $d$  electrons and Al has  $s$  electrons around the Fermi

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energy. Based on the above discussion, the stacking of these metals should vary the phase shift  $\Phi$ , and lead to the modification of the thin-film magnetism. The difference between  $d$  and  $s$  electrons must clarify the role of  $\Phi$ . Actually, we found that these differences lead to a difference of phase shift. Furthermore, we must regard  $\Phi$  as a function of reciprocal space rather than as a simple constant. Our findings suggest that the magnetic switching between paramagnetism and ferromagnetism within the metal nanofilms can be brought on by controlling the dispersion of the band structure originating from quantum-well states via modulation of interface electronic states.

## II. FORMALISM

The phase model Eq. (1) indicates the conditions under which a standing wave can exist. Previous experiments and density functional theoretical (DFT) calculations showed that the period of oscillation by modification of magnetic properties via quantum-well states is expressed as

$$p = \begin{cases} 1/(1 - k_{Fz}) & (k_{Fz} > 1/2), \\ 1/k_{Fz} & (\text{otherwise}), \end{cases} \quad (3)$$

where  $p$  is the period of oscillation (where thickness of the film is  $d$ ) and  $k_{Fz}$  is the vertical Fermi wave number, i.e., the Fermi wave number of the confined band [13]. Equations (1) and (3) indicate that the confined wave number  $k_z$  reaches Fermi energy periodically depending on the film thickness  $d$  [31] and the phase shift  $\Phi$  is unrelated to the period of oscillation. The following contents will explain the details and show the relationship between the  $\Phi$  and the shape of quantum-well band dispersion, which is important to discuss appearance of the ferromagnetism.

Previous DFT calculations predicted that  $d_{xz,yz}$  electrons are confined at the quantum-well states of Pd(100) films [18,19,23]. These orbital characters express one-dimensional dispersion in the in-plane direction. For these electrons, phase shift  $\Phi$  of the quantum-well states might depend on  $k_x$ ,  $k_y$ , and  $\epsilon$ . Thus, it is necessary to expand the phase model to include  $k_x$  and  $k_y$  (i.e., the wave number of the in-plane direction  $\mathbf{k}_{\parallel}$ ) dependencies. Niklasson *et al.* discussed the relationship between the phase model and band dispersion of  $d_{xz,yz}$  well [18].

First, they define  $k_z(n) = (2\pi n - \Phi)/2d$  from Eq. (3). Then they propose that the  $n$ th energy level of Pd(100) film quantum well  $\epsilon_{\text{QW}}(n, \mathbf{k}_{\parallel})$  can be obtained from the Pd bulk energy band structure  $\epsilon(k_z, \mathbf{k}_{\parallel})$  as

$$\epsilon_{\text{QW}}(n, \mathbf{k}_{\parallel}) = \epsilon(k_z(n), \mathbf{k}_{\parallel}), \quad (4)$$

where  $\mathbf{k}_{\parallel} = (k_x, k_y)$  is the in-plane wave vector because the band dispersion of the quantum-well states is a projection of the specific bulk band. Then, the binding energy of the quantum-well state  $\epsilon_{\text{QW}}$  in Pd(100) can be described by expanding  $\epsilon_{\text{QW}}$  around the Fermi energy as

$$\begin{aligned} \epsilon_{\text{QW}}(n, \mathbf{k}_{\parallel}) \sim & \epsilon_{\text{F}} + [k_z(n) - k_{Fz}] \frac{\partial \epsilon}{\partial k_z}(k_{Fz}, \mathbf{k}_{F\parallel}) \\ & + \Delta \mathbf{k}_{\parallel} \cdot \frac{\partial \epsilon}{\partial \mathbf{k}_{\parallel}}(k_{Fz}, \mathbf{k}_{F\parallel}), \end{aligned} \quad (5)$$

where  $\mathbf{k}_{F\parallel}$  is the in-plane Fermi wave vector,  $\Delta \mathbf{k}_{\parallel} = \mathbf{k}_{\parallel} - \mathbf{k}_{F\parallel}$ , and  $\epsilon_{\text{F}} = \epsilon(k_{Fz}, \mathbf{k}_{F\parallel})$ .

Considering Pd bulk band dispersion, dispersion of  $d_{xz,yz}$  has a flat shape around  $\Gamma$  point and zone edges. Therefore, in Pd(100) film, the following relation is satisfied:

$$\frac{\partial \epsilon}{\partial \mathbf{k}_{\parallel}}(k_{Fz}, \mathbf{k}_{F\parallel}) \sim 0. \quad (6)$$

According to Eq. (5), this means that  $\epsilon_{\text{QW}}(n, \mathbf{k}_{\parallel})$  almost coincides with the Fermi energy  $\epsilon_{\text{F}}$  being independent of  $\mathbf{k}_{\parallel}$ , if  $k_z(n)$  matches  $k_{Fz}$ . Then the density of states at the Fermi energy  $D(\epsilon_{\text{F}})$  diverges and induces ferromagnetism from the standpoint of the Stoner criterion [Eq. (2)]. The condition  $k_z(n) = k_{Fz}$  leads to oscillatory appearance of ferromagnetism with the periodicity  $p$  depending on the film thickness  $d$  as described in Eq. (3).

Now we extend the theory above as will be discussed later, the phase shift  $\Phi$  generally depends on  $\mathbf{k}_{\parallel}$ . If we permit such  $\mathbf{k}_{\parallel}$  dependence for  $\Phi$ ,  $k_z(n)$  also depends on  $\mathbf{k}_{\parallel}$ . Since  $k_z(n, \mathbf{k}_{\parallel}) = (2\pi n - \Phi(\mathbf{k}_{\parallel}))/2d$  Eq. (5) must be modified into

$$\begin{aligned} \epsilon_{\text{QW}}(n, \mathbf{k}_{\parallel}) \sim & \epsilon_{\text{F}} + [k_z(n, \mathbf{k}_{F\parallel}) - k_{Fz}] \frac{\partial \epsilon}{\partial k_z}(k_{Fz}, \mathbf{k}_{F\parallel}) \\ & + \Delta \mathbf{k}_{\parallel} \cdot \frac{\partial \epsilon}{\partial \mathbf{k}_{\parallel}}(k_{Fz}, \mathbf{k}_{F\parallel}) \\ & + \Delta \mathbf{k}_{\parallel} \cdot \frac{\partial k_z}{\partial \mathbf{k}_{\parallel}}(n, \mathbf{k}_{F\parallel}) \frac{\partial \epsilon}{\partial k_z}(k_{Fz}, \mathbf{k}_{F\parallel}). \end{aligned} \quad (7)$$

Because of the fourth term on the right-hand side of Eq. (7),  $\epsilon_{\text{QW}}(n, \mathbf{k}_{\parallel})$  is no longer the constant for  $\mathbf{k}_{\parallel}$  and the divergence of  $D(\epsilon_{\text{F}})$  does not occur often, even when  $k_z(n, \mathbf{k}_{F\parallel})$  matches  $k_{Fz}$  and Eq. (6) is satisfied. Furthermore, the divergence of  $D(\epsilon_{\text{F}})$  can be promoted if we appropriately modify the  $\mathbf{k}_{\parallel}$  dependence of  $\Phi$  even when  $k_z(n, \mathbf{k}_{F\parallel})$  does not match  $k_{Fz}$  or Eq. (6) is not satisfied. Thus, we can expect that a fine control of the  $\mathbf{k}_{\parallel}$  dependence of phase shift  $\Phi$  can reduce the magnetism in a similar way to induce the magnetism for nonmagnetic materials. We note that in Eq. (7), the case of  $k_{Fx} = k_{Fy} = 0$  is special. From time-reversal symmetry, the first term of Taylor expansion is disappeared when  $k_{Fx} = k_{Fy} = 0$ . Thus, we have to consider about the higher term of Taylor expansion. Nevertheless, we can use same approach [i.e., considering the fourth term of Eq. (7)] for flat shape band structure of QWs.

To verify this theory, we simulated modification of the interface electronic states of a Pd(100) quantum well using hybridization of the wave functions by making a transition metal/Pd interface. We focused on stacking of the Au monolayer, which is well studied for Pd, and expected interaction of the magnetic  $d$  electrons [32,33]. The Al/Pd(100) system is also simulated to compare the effects of  $d$  electrons and  $s$  electrons using the DFT calculation.

## III. METHOD

All DFT calculations were performed with PHASE/0 code [34] using the projector augmented wave [35] to the spin-polarized local density approximation reported by Perdew and Wang [36]. The  $60 \times 60 \times 1$   $k$  points and 36 Ry of cutoff energy were used. The values of the lattice constant converge

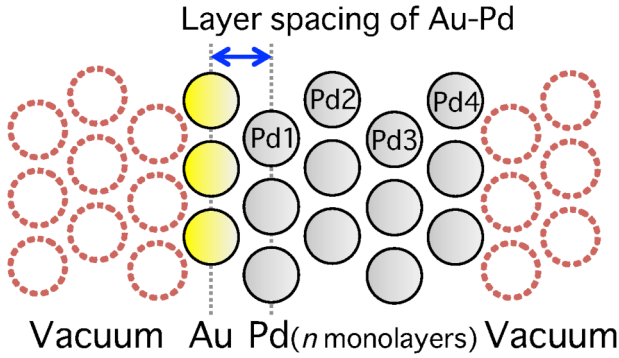


FIG. 1. A schematic image of the slab model of present calculations.

to 0.384 nm for fcc bulk Pd, and we used this value for film-shaped Pd(100). Pd(100) ultrathin films express ferromagnetism in an oscillatory manner depending on the layer thickness, and the period of oscillation is 5–6 monolayers of Pd (for example, 4, 9, 10, and 15 monolayers Pd(100) show ferromagnetism: See Ref. [26] in Fig. 3). In the present study, the magnetism and electronic states of Au and Al stacked Pd(100) ultrathin films using the slab model in Fig. 1 are calculated. We adjusted the out-of-plane lattice spacing between the stacking layer and Pd to adjust the hybridization of the wave function at the interface of the Pd quantum well. By total energy minimization for the free parameter of the interlayer distance of Au-Pd and Al-Pd, we found the converged values of 0.205 and 0.163 nm, respectively (see Appendix B).

Our present obtained lattice constant of 0.384 nm for bulk Pd is smaller than the experimentally observed one of 0.389 nm. Basically, the magnetic ground state of Pd is sensitive to lattice constant. Reference [12] shows that the method for volume correction to obtain good agreement with experiment of both lattice constant and magnetic ground state of Pd. On the other hand, our previous papers show that our present method using freestanding Pd slab with lattice constant of 0.384 nm obtained from the normal LDA method well reproduces the experimentally observed quantum-well-induced ferromagnetism (Refs. [20,25,26]). Thus, in this pa-

per, we use this requirement in order to discuss the quantum-well-induced ferromagnetism using a simple method.

#### IV. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show the layer spacing of Au-Pd-dependent magnetic moment of Au (one monolayer)/Pd (three monolayers) and Au (one monolayer)/Pd (four monolayers), which exhibit nonmagnetism and ferromagnetism, respectively, when they are freestanding Pd(100). The magnetic moment of Pd layers is altered by changing the Au-Pd layer spacing. Although we also have calculated the magnetism of a Au/Pd (two, five, and six monolayers) system, the Pd layers were nonmagnetic despite changing Au-Pd layer spacing. We emphasize that the ferromagnetism that appeared in Au/Pd (three monolayers) and disappeared in Au/Pd (four monolayers) by moving the Au layer closer to the Pd film. This phenomenon indicates, as it were, increase in the effective film thickness of quantum-well-induced ferromagnetism in Pd films by moving of the Au layer closer to Pd, in comparison to the freestanding Pd(100) films. In addition, as shown in Fig. 2(c), not only at the interface of Au/Pd, but also in all layers of the Pd films, the magnetism was modified by modification of the interface electronic states. This indicates that changes in interface electronic states affects the entire film.

Previous calculation shows that the charge transfer to Pd(100) films can modify the magnetism of Pd [22,23]. By contrast, the present result is not explained by a charge transfer from Au to Pd. From the previous calculation, a surface carrier density  $\Delta\sigma$  greater than  $2.8 \times 10^{13} \text{ cm}^{-2}$  is necessary to cancel the ferromagnetic state in four-monolayer Pd(100) film [23]. In the present calculation, we estimate the charge transfer between Au and Pd by comparing the charge distribution of pure Au and pure Pd films, and of the layer-spacing-dependent change of the Au/Pd film system. Consequently, the occurrence of charge transfer from Au to Pd was less than half the amount necessary to cancel ferromagnetism of these films.

To investigate the origin of the change in the magnetism of Pd films by Au stacking effect, we calculated the density of

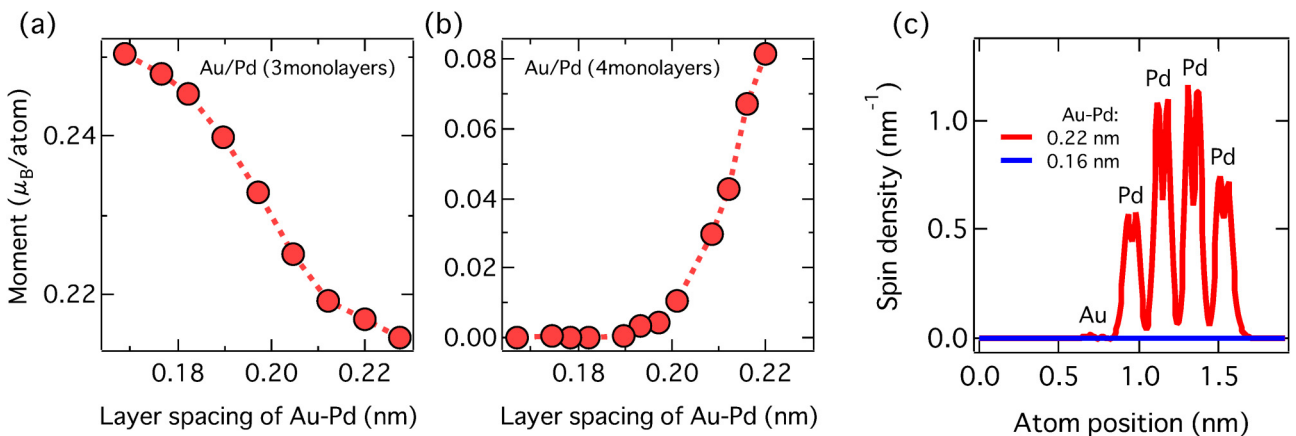


FIG. 2. The layer spacing of Au-Pd dependent magnetic moment of (a) Au/Pd (three monolayer) system and (b) Au/Pd (four monolayer) system; (c) The layer spacing of Au-Pd-dependent spin density in the Au/Pd (four monolayers) slab.

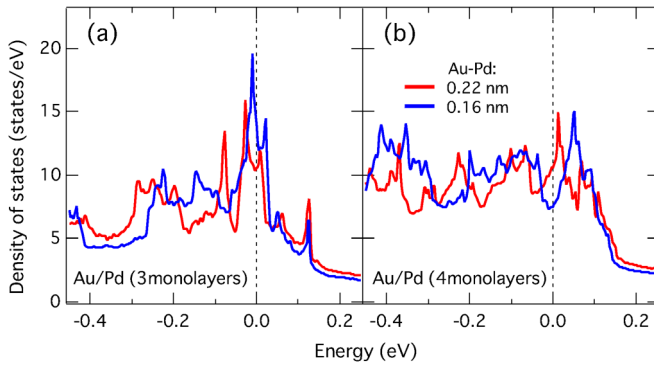


FIG. 3. The layer spacing of Au-Pd dependent on the density of states around the Fermi energy of (a) Au/Pd (three monolayer) system and (b) Au/Pd (four monolayer) system.

state of Au/Pd film systems depending on the layer spacing of Au-Pd [Figs. 3(a) and 2(b)]. The  $D(\epsilon_F)$  increases with decrease of the layer spacing between Au-Pd in a Au/Pd-three-

monolayer system. In contrast, in Au/Pd-four-monolayer system, decrease in  $D(\epsilon_F)$  by increase in the Au-Pd layer spacing was observed. It is known that the magnetic order in metals is determined by the electronic states around the Fermi energy, and that the condition for appearance of ferromagnetism is described as the Stoner criterion, Eq. (2). From the standpoint of the Stoner criterion, modification of  $D(\epsilon_F)$  changes in the stability of the ferromagnetic order. Thus, the disappearance of ferromagnetism by decrease in the Au-Pd layer spacing in a four-monolayer Pd system is explained from the standpoint of the Stoner criterion.

To discuss the change in  $D(\epsilon_F)$  caused by moving the Au layer closer to Pd films, we calculated the band dispersion. Figures 4(a) and 4(b) show the band dispersion of the Au/Pd (three monolayers) with 0.22 and 0.16 nm, of layer spacing of Au-Pd, respectively. We verified the effect of hybridization of wave functions between Au and Pd by comparing the band dispersion of freestanding three-monolayer Pd(100) and Au monolayer [Figs. 4(c) and 4(d)], respectively. The band dispersion that originated from the  $d$ -electron quantum-well

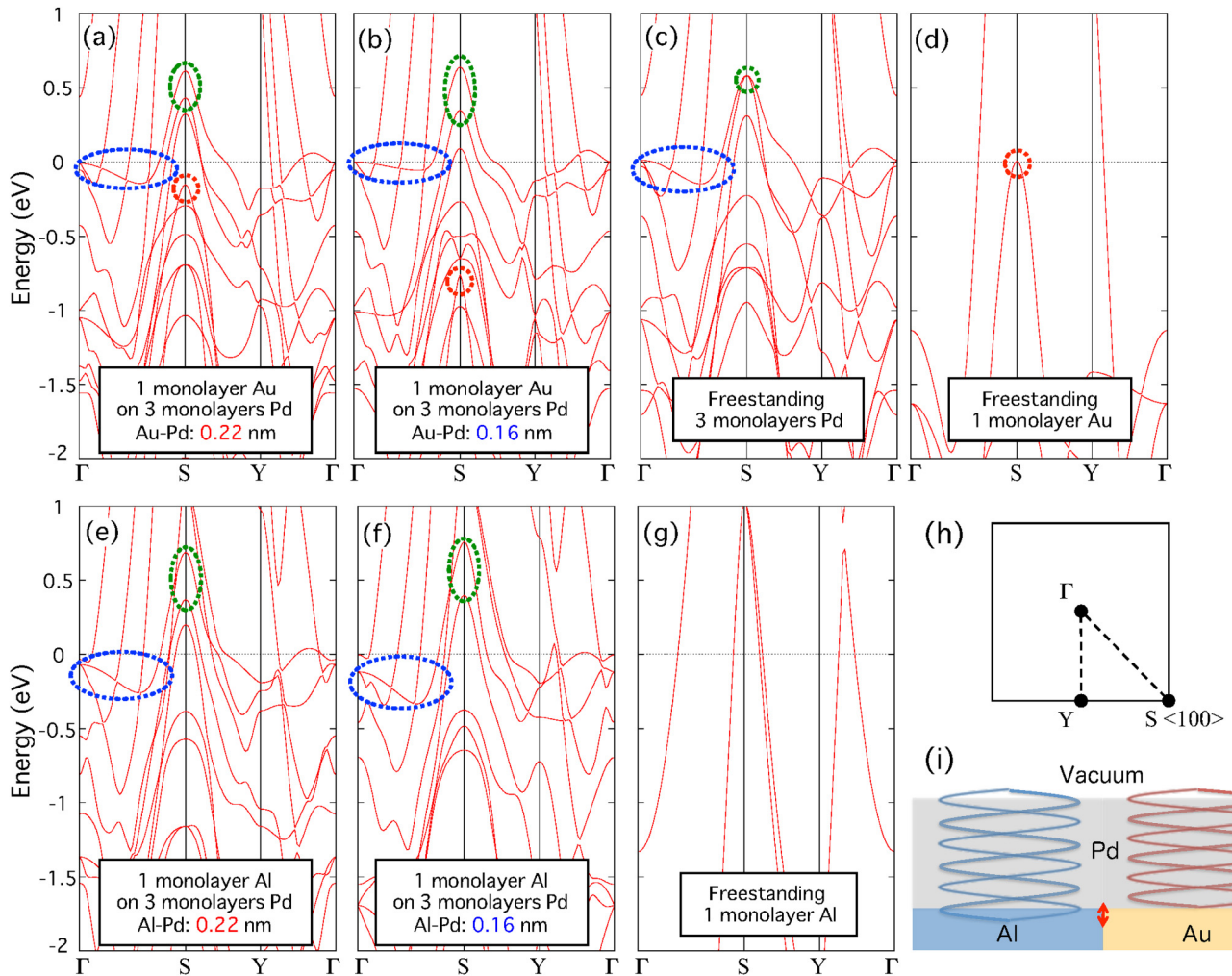


FIG. 4. Band dispersions of Au/Pd (three monolayers) system with (a) 0.22 nm and (b) 0.16 nm of Au-Pd layer spacing. Band dispersion of (c) freestanding three monolayers Pd(100) and (d) one monolayer Au. Band dispersions of Al/Pd (three monolayers) system with (e) 0.22 nm and (f) 0.16 nm of Al-Pd layer spacing; (g) Band dispersion of freestanding one monolayer Al; (h) Two-dimensional Brillouin zone and the high symmetry points of Pd(100) films; (i) A schematic image of the change in interface scattering phase shift.

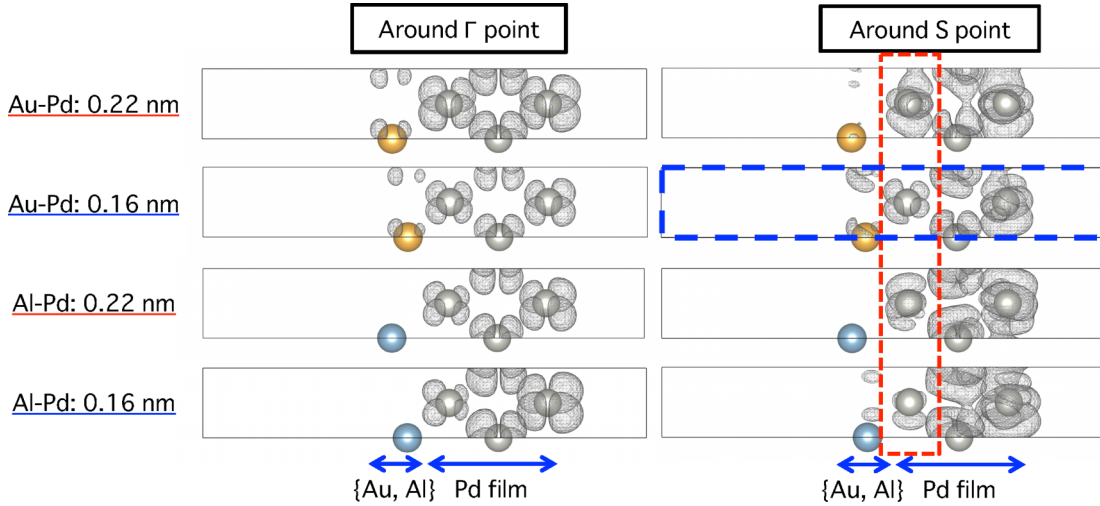


FIG. 5. Layer spacing of (Au, Al)-Pd films dependent on wave function of the quantum-well states of Pd around  $\Gamma$  and S point.

states of Pd are clearly observed on  $\Gamma$ -S line defined in Fig. 4(h) [blue circle in Figs. 4(a)–4(c)] [23]. In the case of freestanding Pd film,  $\mathbf{k}_{F\parallel} = (k_{F_x} = 0, k_{F_y} = 0)$  matches with our formalism in Sec. II. Although the necessary here band dispersion that originated from quantum-well states degenerated at the S point in freestanding Pd film [green circle in Fig. 4(c)], the degeneracy was avoided in Au/Pd system due to its broken symmetry [green circle in Figs. 4(a) and 4(b)].

There is a  $d$ -electron band around Fermi level at S point in monolayer Au [red circle in Fig. 4(d)]. It is, thus, expected that interaction between the Au and  $d$ -electron quantum-well states of Pd films would occur at S point. Actually, value of band splitting of Pd quantum-well band at S point becomes larger as Au layer moves closer to Pd [green circle in Figs. 4(a) and 4(b)]. In addition, binding energy of  $d$ -electron band of Au [which exists around S point in Au/Pd(100) system; red circle in Figs. 4(a) and 4(b); and of which we confirmed the character of band to see the wave function] becomes larger as Au moves closer to the Pd films. These phenomena suggest occurrence of a hybridization of wave function between  $d$  electrons of Au and  $d$ -electron quantum-well states in Pd. The hybridization becomes larger as the Au layer moves closer to Pd. This hybridization induces modification (flattening) of band dispersion originating from quantum-well states. This phenomenon indicates that there is interaction at S point, but no interaction at  $\Gamma$  point, and that removal of quantum-well band in Pd film only occurred around S point, i.e., modification of quantum-well band depends on  $\mathbf{k}_{\parallel}$ . According to Eq. (7), modification of shape of the quantum-well band dispersion is well explained by the change in phase shift  $\Phi$ , and this indeed depends on  $\mathbf{k}_{\parallel}$ . This increase in flatness of band dispersion increased  $D(\epsilon_F)$  of system. The change of density of states [Fig. 3(a)], therefore, is well explained.

To evaluate the effect of hybridization of Au and Pd quantum-well bands, the wave functions were calculated. Figure 5 shows the wave function of quantum-well band of Pd (blue circle in Fig. 4) around the  $\Gamma$  and S points drawn on the slab model. At  $\Gamma$  point, all orbital characters are allowed to exist. Quantum-well states of Pd originated from confinement of  $d_{xz,yz}$  orbital character [37], and we observed these orbital

characters in Pd around  $\Gamma$  point. By contrast, around S point, electronic states should be derived mostly from  $d_{x^2+y^2}$  orbital, due to the requirement for symmetry. Focusing on the Pd layer adjacent to the Au layer (red dashed square), although the  $d_{x^2+y^2}$  orbital character of Pd was observed around the S point when Au layer was far from Pd layer (0.22 nm),  $d_{xz,yz}$  orbital-like character was observed when Au was moved closer to the Pd layer (0.16 nm, blue dashed square). In addition, when the distance between Au-Pd layers was 0.16 nm, the wave function of Au layer (which is hybridized with quantum-well band in Pd) showed  $d_{x^2+y^2}$ - $p_{x,y}$  hybridized orbital character (Fig. 5). This phenomenon clearly suggests hybridization between wave function of Au and quantum-well band in Pd films around S point at Au/Pd interface. This causes the change in band dispersion of quantum-well states. Evidence of hybridization between  $d$  electrons in Au and Pd quantum-well states is also indicated by spin density in Fig. 2(c). Au layer shows a small amount of spin polarization when quantum-well-induced ferromagnetism appears in Pd(100). Au is a typical nonmagnetic transition metal, therefore the spin polarization in Au layer of Au/Pd(100) system is caused by hybridization between Au and magnetic Pd  $d$  electrons.

This interaction of quantum-well states depending on position of reciprocal lattice space is caused by a stacking layer having  $d$  electrons (i.e., Au). In fact, the same effect is observed in a system in which an Fe monolayer is stacked on four-monolayer Pd(100). Layer spacing of Fe-Pd converges to 0.169 nm, and all of Pd layers show spin polarization at that time. In contrast, only Pd layer adjacent to Fe layer shows ferromagnetism (proximity-induced magnetism) when layer spacing of Fe-Pd is 0.192 nm (the lattice constant of Pd). Thus, our finding is that magnetic change generally occurs when a  $d$ -electron transition metal is stacked on Pd(100) films. Here, the system with stacked Al (which has only  $s$  electrons at the Fermi energy) on the three-monolayer Pd(100) is also discussed to compare it with  $d$ -transition metals. Although the Fermi level of Pd is modified by the charge transfer from Al, which erase the ferromagnetism, the shape of band dispersion is not altered by changing Al-Pd layer spacing [Figs. 4(e)–4(g)]. Symmetry of orbital character of quantum-well states

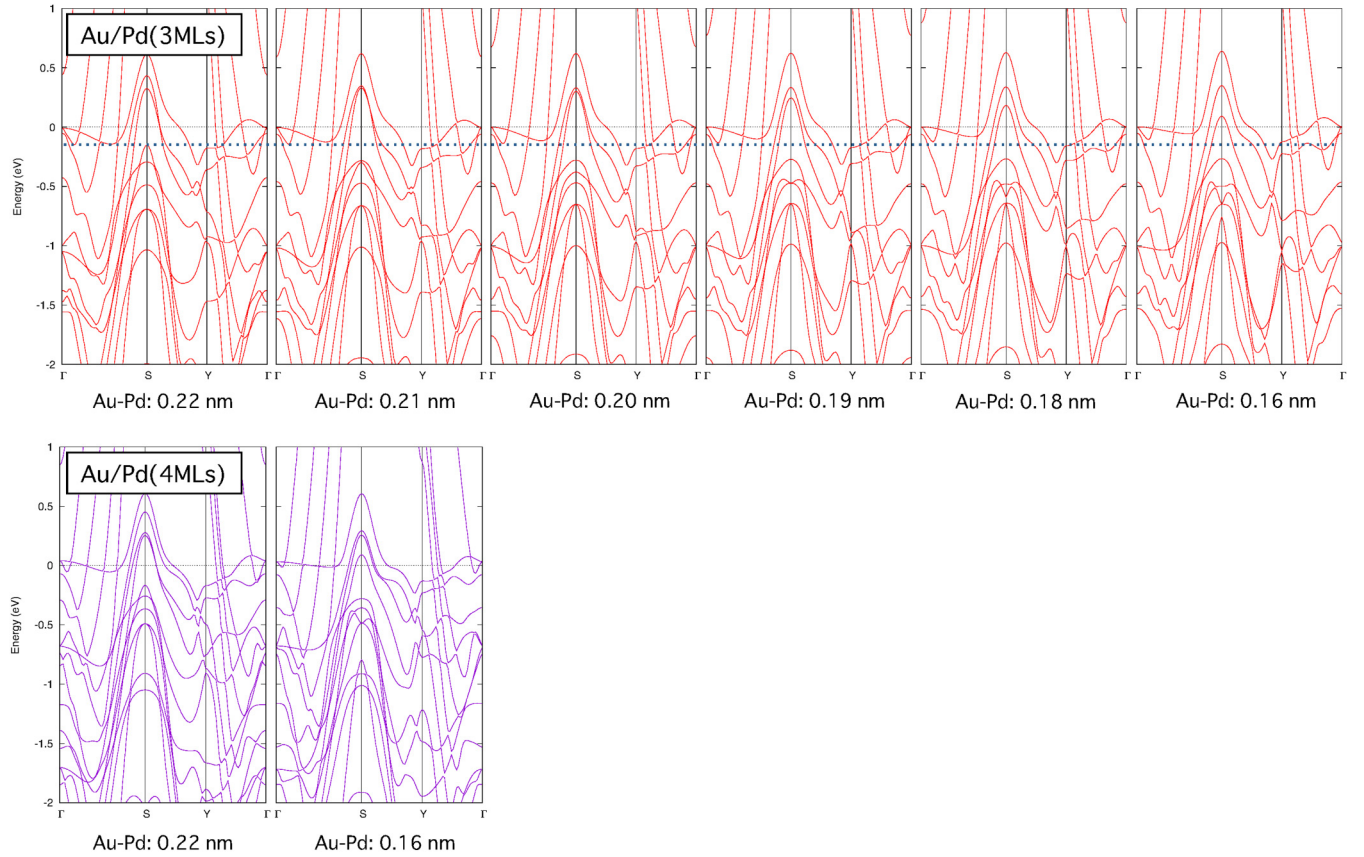


FIG. 6. Band dispersions of Au/Pd (three and four monolayers: MLs) system with from 0.22–0.16 nm of the Au-Pd layer spacing. The lattice constant of Pd is fixed to the bulk converged value.

of Pd films are also not modified in relation to Al-Pd layer spacing around S point (Fig. 5). This indicates that there is no hybridization between the Al  $s$  band and  $d$ -electron quantum-well band of Pd films. The final term of Eq. (7) is zero in case of Al stacking system. On the other hand, systems with Au stacking is nonzero. This, therefore, suggests that adsorption of a transition metal having  $d$  electrons is essentially important to control quantum-well-induced ferromagnetism using modulation of shape of band dispersion of quantum-well bands, i.e., the effect of the modification of  $\Phi$  depending on  $k_{\parallel}$ . From Eq. (1), this phenomenon discussed here is interpreted that the change in effective thickness of quantum well occurs only around the Au-stacked S point [Fig. 4(i)].

According to the phase model in Eq. (1) and our newly obtained Eq. (7), enhancement of flatness of band dispersion originating from quantum-well states around the zone edge

indicates the modification in phase shift  $\Phi$ , which indeed depends on  $k_{\parallel}$ . Our present DFT calculations show that the  $d$ -electron quantum-well-induced ferromagnetism is controlled by the change at interface electronic states via stacking of an overlayer having  $d$  electrons. Hitherto, the term  $\Phi$  was just a parameter for describing the quantum-well states in real space. Our present DFT calculation suggests a mechanism by which to control the term in  $\Phi$  as a function of position of reciprocal lattice point. Thus, our finding extends the interface effect of quantum-well states. This mechanism indicates the possibility of controlling over electronic states in whole films using the effect from hybridization of wave functions due to modification of interface electronic states of metal-nanofilm structures.

We note that our previous studies show that the model of freestanding Pd slab, which is used also in this study,

TABLE I. Out-of-plane lattice constant of Au/Pd (2–6 monolayers: MLs). There is no change in the in-plane lattice constants from bulk converged value.

	Moment ( $\mu_B/\text{Pd}$ )	Au-Pd1(nm)	Pd1-Pd2(nm)	Pd2-Pd3(nm)	Pd3-Pd4(nm)	Pd4-Pd5(nm)	Pd5-Pd6(nm)
Au/Pd (2 MLs)	0.00	0.205	0.189				
Au/Pd (3 MLs)	0.23	0.205	0.194	0.189			
Au/Pd (4 MLs)	0.00	0.204	0.193	0.191	0.189		
Au/Pd (5 MLs)	0.00	0.205	0.194	0.192	0.191	0.189	
Au/Pd (6 MLs)	0.00	0.205	0.194	0.194	0.192	0.192	0.189

TABLE II. Out-of-plane lattice constant of Al/Pd (2–6 monolayers: MLs). There is no change in the in-plane lattice constants from bulk converged value.

	Moment ( $\mu_B/\text{Pd}$ )	Al-Pd1 (nm)	Pd1-Pd2 (nm)	Pd2-Pd3 (nm)	Pd3-Pd4 (nm)	Pd4-Pd5 (nm)	Pd5-Pd6(nm)
Al/Pd (2 MLs)	0.00	0.162	0.197				
Al/Pd (3 MLs)	0.00	0.162	0.202	0.190			
Al/Pd (4 MLs)	0.00	0.162	0.201	0.193	0.189		
Al/Pd (5 MLs)	0.00	0.162	0.200	0.194	0.192	0.188	
Al/Pd (6 MLs)	0.00	0.162	0.201	0.193	0.192	0.191	0.188

well explains the quantum-well-induced ferromagnetism in Pd films [20,25,26]. In addition, we also see the stacking effect for quantum-well states discussed in this paper in the sufficiently thick film to perform the experiment. Thus, we would expect the control over magnetism predicted here to be experimentally observable in a Au/Pd system on a piezo substrate. In this system, the change in the out-of-plane lattice constant occurs via occurrence of piezo effect in the in-plane lattice constant, by which modification of Au-Pd layer spacing is realized. The previous experiment and DFT calculation showed evidence for the control of magnetic moment in pure Pd(100) films via lattice distortion from a ferroelectric BaTiO<sub>3</sub> substrate [25]. The lattice expansion induced by the lattice distortion of the substrate causes narrowing of density of states in bulk band and changes its magnetic properties [26,38–42]. However, in pure Pd(100) ultrathin films on a BaTiO<sub>3</sub> substrate, the amount of change in magnetic moment was only 5%. Our present DFT calculation suggests that modification of band dispersion that originates from quantum-well states will produce a synergistic effect capable to alter the magnetism by lattice distortion using Au/Pd/piezo-substrate heterostructure. Using this mechanism, it is expected that nonmagnetic to ferromagnetic switching could be provided by applying lattice distortion in quantum-well-induced ferromagnetism.

In the case of quantum confinement of Pd  $d_{xz,yz}$  electrons, which we discussed in this paper, the hybridization between the  $d$ -electron wave function of the stacking layer and Pd at the zone edge (S point) is intrinsically important for producing a flat band. Because typical 3, 4, 5d transition metals forming fcc structure have  $d$ -electron bands around the S point, this effect generally occurs by stacking of these transition metals on Pd(100) films. In addition, if the  $d$ -electron band of a stacking layer appears near the Fermi energy at S point, magnetic change might be clearly observed, as indicated in Eq. (7).

## V. CONCLUSIONS

In conclusion, the magnetic change in Pd(100) ultrathin films with quantum-well-induced ferromagnetism caused by the stacking effect of transition metal was investigated using DFT calculation. When a Au layer with  $d$  electrons was stacked on  $d$ -electron quantum-well, change in the quantum-well-induced ferromagnetism was observed. This phenomenon is explained by modification of the term of the interface scattering phase shift  $\Phi$  as a function of reciprocal lattice space via hybridizing of wave functions between band dispersion in stacking  $d$ -electron and  $d$ -electron

quantum-well states. In the case of confined  $d_{xz,yz}$  electrons, modification of  $\Phi$  only occurred around the zone edge, and the dispersion shape flattened (i.e., the density of the states was modified). Contrastingly, we observed that stacking of Al, which contains only  $s$  electrons around Fermi energy, cannot modify the shape of the band dispersion of  $d$ -electron quantum-well states because there is no hybridization between the  $s$  and  $d$  electrons. Our findings suggest a mechanism for controlling magnetism using modification of interface electronic states in metal-nano structures. This mechanism could be extended to other magnetic materials. This creates the possibility of tailoring magnetic materials by appropriate electronic engineering of interface structure.

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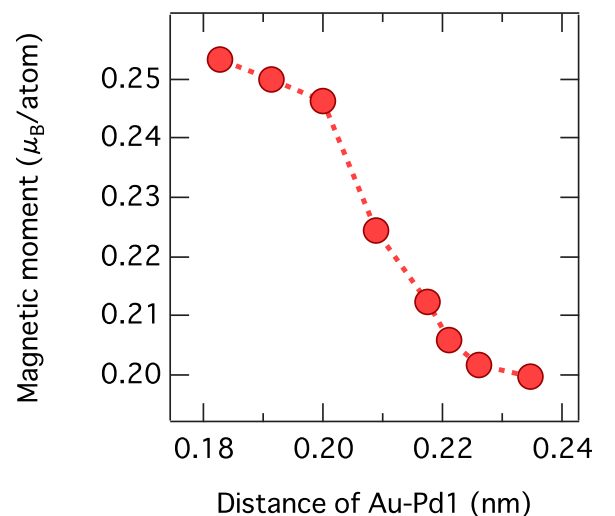


FIG. 7. The layer spacing of Au-Pd dependent the magnetic moment of Au/Pd (three monolayer) system with Pd structure obtained from full structural relaxations.

## APPENDIX A: AU-PD DISTANCE DEPENDENCE OF QUANTUM-WELL STATES

In Fig. 4, we show the change in quantum-well states of Pd(100) ultrathin film with 0.22 nm and 0.16 nm of Au-Pd layer spacing. In Fig. 6, we show band dispersion of Au/Pd (three monolayers) system with various Au-Pd layer spacing. We can see the gradual changes of quantum-well band dispersion of Pd films depending on the Au-Pd layer spacing. In addition, we note that we can see the same result in Au/Pd (four monolayers) system.

## APPENDIX B: FULL STRUCTURAL RELAXATIONS OF AU/PD (2-6 MONOLAYERS) AND AL/PD (2-6 MONOLAYERS)

To discuss the magnetic ground states, we should consider the film structure because the magnetism in Pd is sensitive to the lattice parameter. Thus, we perform the full struc-

tural relaxations of Au/Pd (2–6 monolayers) and Al/Pd (2–6 monolayers) systems (Table I and II). As a result, the in-plane lattice dimensions are not changed, but the out-of-plane lattice dimensions are modified. We note that there is no Pd thickness dependence of layer spacing of Au-Pd and Al-Pd. After the full structural relaxations, the stability of magnetic states is a little bit modified, and we cannot see the magnetic moment in Au/Pd (four monolayers) system. On the other hand, we see the spontaneous magnetization of Pd in Au/Pd (three monolayers) system even in the lattice parameter obtained from the full structural relaxations. Then, we fixed Pd-Pd layer spacing to the values obtained from the full structural relaxations, and we checked the Au-Pd layer spacing dependence of magnetism for Au/Pd (three monolayer) system (Fig. 7). As a result, we see the same behavior as Fig. 2(a). We note that we cannot see the ferromagnetic order in Al/Pd (three monolayers) system when we modified the Al-Pd distance. Therefore, our present summary is satisfied even in the system with full structural relaxations.

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