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).

I. INTRODUCTION

For the development of novel electronic devices based on the spin degree of freedom of electrons, the switching of the magnetic order of the materials using external fields is an idea having the potential to update the concept of current magnetic memory devices. Recently, it was experimentally shown that the magnetism and magneto anisotropy of Fe, Co, and Pt ultrathin films and the proximity-induced magnetism of Pd and Pt ultrathin films, could be modulated using an external field. An experiment involving X-ray magnetic circular dichroism and first-principle 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, and change in the electric quadrupole.

However, in the metal ultrathin film systems used in the electric field effect experiment, the electronic states are modified by the size effect caused by nano-scaling of the metals, and the magnetic states are different from those with bulk metals. The quantum-well states occurring in ultrathin film formed from metal, in particular, modulate the density of states at the Fermi energy in an oscillatory manner depending on the film thickness. The period of oscillation is determined by the Fermi wave number of metals. The confined electronic states in the quantum-well are described by the phase model,

\[ 2k_{\parallel}d + \Phi = 2\pi n, \]

where \( k_{\parallel} \) is the confined wave number, \( d \) is the film thickness, \( \Phi \) is the scattering phase shift at the 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. From this mechanism, the magneto anisotropy of Fe and Co ultrathin films is modulated in addition, ferromagnetism appears in Pd(100) ultrathin films in an oscillatory manner dependent on the film thickness. This quantum-well induced ferromagnetism is modulated by controlling the Fermi level using an electronic field and by modifying the quantum-well states using lattice distortion. The mechanism by which these control the magnetism is well understood from the viewpoint of change in the band dispersion.

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. However, \( \Phi \) is just a parameter in the phase model, and the currently proposed method for controlling \( \Phi \) only involves modifying the work function of the materials. 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 to control the size effect. This will expand the scientific principle upon which is based magnetic switching by band engineering using quantum-well states.

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 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, and furthermore, that 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 nano films can be brought on by controlling the dispersion of the band structure originating from quantum-well states, via modulation of...
the 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

$$p = \pi/k_F,$$

where $p$ is the period of the oscillation (in thickness of the film) and $k_F$ is the Fermi wave number. This equation indicates that the confined wave number $k_z$ reaches Fermi energy periodically depending on the film thickness. The band dispersion of the quantum-well states is a projection of the specific bulk band. The completion of eq. (2) is based on the number of confined electrons being determined by the orbital character of the electrons in bulk form. In this equation, the phase shift $\Phi$ behaves as the parameter for adjusting the Fermi energy.

Previous DFT calculations predicted that the $d_{xz,yz}$ electrons are confined at the quantum-well states of Pd(100) films. These orbital characters express one dimensional dispersion in the in-plane direction. For these electrons, the phase shift $\Phi$ of the quantum-well states might depend on $k_x$ and $k_y$ (i.e., the wave number of the in-plane direction $k_{||}$) dependency. Niklasson et al. well discussed the relationship between the Phase model and band dispersion of $d_{xz,yz}$. Here, we define the Fermi wave number of the in-plane direction $k_{||}$ and $\Delta k_{||} = k_{||} - k_{F||}$. Then, the binding energy of the quantum-well states $\epsilon_{QW}$ in Pd(100) can be described as in the following equation.

$$\epsilon_{QW}(k_z(n), k_{||}) \sim \epsilon_{QW}(k_z(n), k_{F||}) + \Delta k_{||} \frac{\partial \epsilon}{\partial k_{||}}|_{k_z=k_{Fz}}$$

Considering the tight binding model, the band dispersion of $d_{xz,yz}$ has a flat shape around the $\Gamma$ point and zone edges. For the flat band, the following formula is established:

$$\frac{\partial \epsilon}{\partial k_{||}}|_{k_z=k_{Fz}} \sim 0$$

From eq. (1), $k_z(n) = (2\pi n - \Phi)/2d$, and thus, the density of states at the Fermi energy $D(\epsilon_F)$ diverges in an oscillatory manner depending on the film thickness. This divergence induces ferromagnetism from the standpoint of the Stoner criterion, which is the condition required for the appearance of ferromagnetism in transition metals,

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

where $I$ is the exchange integral. The $k_z(n)$ also depends on $\Phi$, which depends on $\epsilon$ and $k_{||}$, as mentioned above. Therefore, the specific thickness showing the divergence of the $D(\epsilon_F)$ is controlled by modifying $\Phi(\epsilon, k_{||})$. In addition, from the $k_z(n) = k_z(n, \epsilon, k_{||})$, the following equation is completed:

$$\epsilon_{QW}(k_z(n), k_{||}) = \epsilon_{QW}(k_{Fz}(n), k_{F||}) + \Delta k_{||} \frac{\partial \epsilon}{\partial k_{||}}|_{k_z=k_{Fz}}$$

$$+ \frac{\partial \epsilon}{\partial k_z}|_{k_z=k_{Fz}} \Delta k_{||} \frac{\partial k_z}{\partial k_{||}}|_{k_z=k_{Fz}}$$

In some cases, the quantum-well band cannot behave as a sufficiently flat shape to diverge $D(\epsilon_F)$ depending on the function of $\Phi(\epsilon, k_{||})$, even if eq. (1) is partially completed. Conversely, eq. (5) indicates that it should be possible to diverge $D(\epsilon_F)$ of the nonmagnetic materials and control the magnetism of metals, if we modify the function of $\Phi(\epsilon, k_{||})$.

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. In addition, we simulated the Al/Pd(100) system to compare the effects of the d-electrons and s-electrons using the DFT calculation.

III. METHOD

All DFT calculations were performed with PHASE/0 code using the projector augmented wave to the spin-polarized local density approximation reported by Perdew and Wang. The $60 \times 60 \times 1$ $k$-points and 36 Ry of cutoff energy were used. The values of the lattice constant converge to 0.384 nm for fcc bulk Pd, and we used this value for film-shaped Pd(100). In this condition, the calculated magnetic state of freestanding Pd(100) ultrathin films well reproduced the quantum-well induced ferromagnetism reported in a previous paper. 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. in Fig. 3). In the present study, we calculated the magnetism and electronic states of Au and Al stacked Pd(100) ultrathin films using the slab model in Fig. 1. 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. The values of the layer spacing of Au-Pd and Al-Pd converged to 0.205 and 0.163 nm, respectively.
IV. RESULTS AND DISCUSSION

Figures 2 (a) and (b) show the layer spacing of the Au-Pd dependent magnetic moment of Au (1 monolayer) / Pd (3 monolayers) and Au (1 monolayer) / Pd (4 monolayers), which exhibit non-magnetism and ferromagnetism, respectively, when they are freestanding Pd(100). The magnetic moment of the Pd layers is modified by changing the Au-Pd layer spacing. Although we also calculated the magnetism of a Au/Pd (2, 5, and 6 monolayers) system, the Pd layers were non-magnetic despite changing of the Au-Pd layer spacing. We emphasize that the ferromagnetism was made to appear in Au/Pd (3 monolayers) and disappear in Au/Pd (4 monolayers) by moving the Au layer closer to the Pd film. This phenomenon indicates occurrence of 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 change in the interface electronic states affects the entire film.

Previous calculation shows that the charge transfer to Pd(100) films can modify the magnetism of Pd. By contrast, the present result of the calculation is not explained by a charge transfer from Au to Pd. From the previous calculation, a surface carrier density $\Delta \sigma$ greater than $2.8 \times 10^{13}$ cm$^{-2}$ is necessary to cancel the ferromagnetic state in four-monolayer Pd(100) film. 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 the ferromagnetism of these films.

To investigate the origin of the change in the magnetism of Pd films by the Au stacking effect, we calculated the density of state of Au/Pd film systems depending on the layer spacing of Au-Pd (Figs. 3 a and b). The $D(\epsilon_F)$ increases with decrease of the layer spacing of Au-Pd in an Au/Pd-3-monolayer system. By contrast, in the Au/Pd-4-monolayer system, decrease in the $D(\epsilon_F)$ 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 the appearance of ferromagnetism is described as the Stoner criterion, eq. (5). From the standpoint of the Stoner criterion, the modification of $D(\epsilon_F)$ causes change in the stability of the ferromagnetic order. Thus, the disappearance of ferromagnetism by decrease in the Au-Pd layer spacing in a 4-monolayer Pd system is explained from the standpoint of the Stoner criterion.

To discuss the change in $D(\epsilon_F)$ from moving the Au layer closer to Pd films, we calculated the band dispersion. Figs. 4 (a) and (b) show the band dispersion of the Au/Pd (3 monolayers) with 0.22 and 0.16 nm, respectively, of layer spacing of Au-Pd. We verified the effect of the hybridization of the wave functions between Au and Pd by comparing the band dispersion of the freestanding 3-monolayer Pd(100) and Au monolayer (Figs. 4 c and d), respectively. The band dispersion that originated from the d-electron quantum-well states of Pd are clearly observed on the Γ-S line defined in Fig. 4 (h) (blue circle in Figs. 4 a to c). Although the band dispersion that originated from quantum-well states degenerated at the S-point in the freestanding Pd film (green circle in Fig. 4 c), the degeneracy was avoided in the Au/Pd system owing to its broken symmetry (green circle in Figs. 4 a and b).

There is a d-electron band around the Fermi level at the S-point in monolayer Au (red circle in Fig. 4 d). Thus, it is expected that interaction between the Au and d-electron quantum-well states of Pd would occur at the S-point. Actually, the value of the band splitting of the Pd quantum-well band at the S-point becomes larger as the Au layer moves closer to Pd (green circle in Figs. 4 a and b). In addition, the binding energy of the d-electron band of Au (which exists around the S-point in the Au/Pd(100) system; red circle in Figs. 4 a and b) and of which we confirmed the character of the band to see the wave function) becomes larger as Au moves closer to the Pd films. These phenomena suggest the occurrence of a hybridization of the wave function between the d-electrons of Au and d-electron quantum-well states in Pd, and that the hybridization becomes larger as the Au layer moves closer to Pd. This hybridization induces modification (flattening) of the band dispersion originating from quantum-well states. This phenomenon indicates that there is interaction at the S-point, but no interaction at the Γ point, and that lifting of the quantum-well band of Pd film only occurred around the S-point. This increase of the flatness of the band dispersion increased the $D(\epsilon_F)$ of the system; thus, the change of the density of states in Fig. 3 (a) is well explained.

To evaluate the effect of hybridization of the Au and...
FIG. 2. The layer spacing of Au-Pd dependent magnetic moment of (a) Au/Pd(3 monolayer) system and (b) Au/Pd(4 monolayer) system; (c) The layer spacing of Au-Pd dependent spin density in the Au/Pd(4 monolayers) slab.

FIG. 3. The layer spacing of Au-Pd dependent the density of states around the Fermi energy of (a) Au/Pd(3 monolayer) system and (b) Au/Pd(4 monolayer) system.

Pd quantum-well bands, we calculated the wave function. Fig. 5 shows the wave function of the quantum-well band of Pd (blue circle in Fig. 4) around the Γ and S points drawn on the slab model. At the Γ point, all the orbital characters are allowed to exist. The quantum-well states of Pd originated from confinement of the \( d_{xz,yz} \) orbital character, and we observed these orbital characters in Pd around the Γ point. By contrast, around the S-point, the electronic states should be derived mostly from the \( d_{x^2-y^2} \) orbital, from 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 the Au layer was far from Pd layer (0.22 nm), \( d_{xz,yz} \) orbital-like character was observed when the Au was moved closer to the Pd layer (0.16 nm, blue dashed square). In addition, when the distance of Au-Pd layer spacing was 0.16 nm, the wave function of the Au layer (which is hybridized with the quantum-well band of Pd) showed \( d_{x+y} \) hybridized orbital character (Fig. 5). This phenomenon clearly suggests the occurrence of hybridization between the wave function of Au and the quantum-well band of Pd films around the S-point at the Au/Pd interface. This induces modification of the band dispersion of the quantum-well states. The evidence of the hybridization between \( d \)-electrons in Au and Pd quantum-well states is also indicated by the spin density in Fig. 2 (c). The Au layer shows a small amount of spin polarization when the quantum-well induced ferromagnetism appears in Pd(100). Au is a typical nonmagnetic transition metal; thus, the spin polarization in the Au layer of the Au/Pd(100) system is caused by the hybridization between the Au and magnetic Pd \( d \)-electrons.

This interaction of the quantum-well states depending on the position of the 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 4-monolayer Pd(100). The layer spacing of Fe-Pd converges to 0.169 nm, and all of the Pd layers show spin polarization at that time. In contrast, only the Pd layer adjacent to the Fe layer shows ferromagnetism (proximity-induced magnetism) when the 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 the Pd(100) films. Here, we also stacked Al (which has only \( s \)-electrons at the Fermi energy), on the 3-monolayer Pd(100) to compare it with \( d \)-transition metals. Although the Fermi level of the band dispersion that originated from the quantum-well states of Pd is modified by the charge transfer from Al, the shape of the band dispersion is not modified by changing the Al-Pd layer spacing (Figs. 4 e to g). The symmetry of the orbital character of the quantum-well states of Pd films are also not modified in relation to the Al-Pd layer spacing around the S-point (Fig. 5). This indicates that there is no hybridization between the Al \( s \)-band and \( d \)-electron quantum-well band of the Pd films. Therefore, it is suggested that adsorption of a transition metal having \( d \)-electrons is essentially important to control quantum-well induced ferromagnetism using modulation of the shape of the band dispersion of
the quantum-well bands (Fig. 4 i).

According to the phase model in eq. (1) and (3), enhancement of the flatness of the band dispersion originating from the quantum-well states around the zone edge, indicates the occurrence of modification in the phase shift $\Phi$. Our present DFT calculations show that the $d$-electron quantum-well-induced ferromagnetism is controlled by change at the 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 the real space. Our present DFT calculation suggests a mechanism by which to control the term of $\Phi$ as a function of the position of the reciprocal lattice point. Thus, our finding extends the interface effect of the quantum-well states, which was only understood in real space, from the standpoint of the reciprocal lattice space. This mechanism indicates the possibility of controlling the electronic states in whole films using the effect from hybridization of wave functions because of modification of the interface electronic states of the metal-nano film structures.

We would expect the control of 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 the piezo effect on the in-plane lattice constant, by which modification of the Au-Pd layer spacing is realized. The previous experiment and DFT calculation showed evidence of control of the magnetic moment in pure Pd(100) films via lattice distortion from a ferroelectric BaTiO$_3$ substrate. The lattice expansion induced by the lattice distortion of the substrate causes narrowing of the density of states of the bulk band, and changes its magnetic properties. However, in the pure Pd(100)
ultrathin films on a BaTiO₃ substrate, the amount of change in the magnetic moment was only 5%. Our present DFT calculation suggests that modification of the band dispersion that originates from the quantum-well states will produce a synergistic effect able to alter the magnetism by lattice distortion using the Au/Pd/piezostack heterostructure. Using this mechanism, it is expected that nonmagnetic to ferromagnetic switching could be provided by applying lattice distortion in the quantum-well-induced ferromagnetism.

In the case of the quantum confinement of the Pd dₓz,ᵧz 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 the S-point, the magnetic change might be clearly observed, as indicated in eq. (3).

V. CONCLUSIONS

In conclusion, we investigated the magnetic change in Pd(100) ultrathin films with quantum-well induced ferromagnetism caused by the stacking effect of the transition metal using the DFT calculation. When a Au layer with d-electrons was stacked on the d-electron quantum-well, modification of the quantum-well induced ferromagnetism was observed. This phenomenon is explained by modification of the term of the interface scattering phase shift Φ as a function of the reciprocal lattice space via hybridizing of the wave functions between the band dispersion of the stacking d-electron and d-electron quantum-well states. In the case of confined dₓz,ᵧz electrons, modification of Φ only occurred around the zone edge, and the dispersion shape flattened (i.e., the density of the states was modified). Contrastingly, we observed that the stacking of Al, which contains only s-electrons around Fermi energy, cannot modify the shape of the band dispersion of the 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 the interface electronic states in metal-nano structures. This mechanism could be extended to other magnetic materials, creating the possibility of tailoring magnetic materials by appropriate electronic engineering of the interface structure.

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