Thickness-dependent appearance of ferromagnetism in Pd(100) ultrathin films

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We report the appearance of ferromagnetism in thin films of Pd(100), which depends on film thickness in the range of 3–5 nm on SrTiO$_3$(100) substrates. X-ray magnetic circular dichroism measurement shows the intrinsic nature of ferromagnetism in Pd(100) films. The spontaneous magnetization in Pd(100) films, corresponding to is 0.61μ_B/atom, is comparable to Ni, and it changes in an oscillatory manner depending on film thickness, where the period quantitatively agrees with the theoretical prediction based on the two-dimensional quantum well in the film. This indicates that the discrete electronic states in the quantum well shift to Fermi energy to satisfy the condition for ferromagnetism (Stoner criterion) at a specific film thickness.

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I. INTRODUCTION

The appearance of ferromagnetism in typical metals is predicated upon a materials electronic structure through the Stoner criterion [1]

$$ID(\epsilon_F) > 1, \tag{1}$$

where I is the exchange integral and $D(\epsilon_F)$ is the density of states (DOS) at Fermi energy. One interesting example of using the Stoner criterion is a nanosized metal whose magnetism is sensitive depending on its size. This is because the change in electronic structure and discreteness of the electronic state due to miniaturization can significantly modulate DOS at Fermi energy. Many recent reports show that nonmagnetic metals in bulk can change into ferromagnets in nanoparticles [2–6], thus proving the effectiveness of the theoretical prediction. For example, Pd nanoparticles show ferromagnetism [2,3,7–9]. Spontaneous magnetization corresponding to $0.75 \pm 0.31\mu_B$/atom appearing from the topmost 2–5 layers on (100) facets of the Pd nanoparticle has been reported [3]. Such ferromagnetism can be interpreted in terms of the electronic structure through Stoners criterion [1]. Many experimental studies concerning ferromagnetism in nanoparticle systems still require qualitative interpretation of the ferromagnetic origin, however, because of the difficulty of evaluating magnetism based on the electronic structure of nanoparticles.

Provided that ferromagnetic ordering can be expected in 4d metal in film form, this can be compared with the calculated electronic structure to identify the magnetic origin. Various researchers have theoretically predicted the appearance of ferromagnetism in Pd(100) thin film based on the energy band calculation [10–16], which is qualitatively consistent with ferromagnetic ordering appearing on the (100) facets of Pd nanoparticles. In addition, some reports indicated that it is the quantum-well (QW) states that appear in nanosized thin film

that induce the change in DOS at Fermi energy, depending on film thickness. Thus, the ferromagnetism appears in an oscillatory manner to film thickness [14–16]. The experimental observation of this behavior presented here gives direct evidence of the validity of the magnetic picture of itinerant ferromagnetism based on electron structure. In addition, it predicts that changes in magnetism can be easily realized by weak perturbation when the film thickness is adjusted around the magnetic boundary [17,18].

In this paper, we report the discovery that palladium, which is nonmagnetic but nearly ferromagnetic in bulk from Stoners standpoint, shows ferromagnetism with large magnetization that oscillates depending on film thickness in (100) thin film with thicknesses of 2.9–5.55 nm on a SrTiO$_3$ (STO) substrate; in addition, the oscillation period agrees well with the first-principles calculation relating to two-dimensional QW states in the electronic structure. Our observations were based on magnetization measurements and x-ray magnetic circular dichroism (XMCD) spectroscopy. This is the observation of systematic change in nanosized metallic magnetism to be quantitatively evaluated based on the change in DOS at Fermi energy in electronic structure as a function of size. The fact that the magnetism of metal undergoes intense change with changing film thickness will open the way to systematically tuning a desired magnetic state in a metal, and enable innovative uses for the magnetic control of metallic materials.

II. EXPERIMENT

We grew epitaxial Pd thin films in a vacuum lower than 1×10^{-9} Torr on the STO substrate which has Ti-O terminated step-and-terrace surface structure (SHINKOSHA Co., Ltd.) [19]. The following three-step growth method [20] was used: one-fifth of the total amount of Pd film was deposited at 573 K, then cooled to room temperature; the rest of Pd was then deposited; finally, it was heated to 500 K. The reflection high-energy electron diffraction (RHEED) image of the deposited Pd thin films showed sharp streaks corresponding
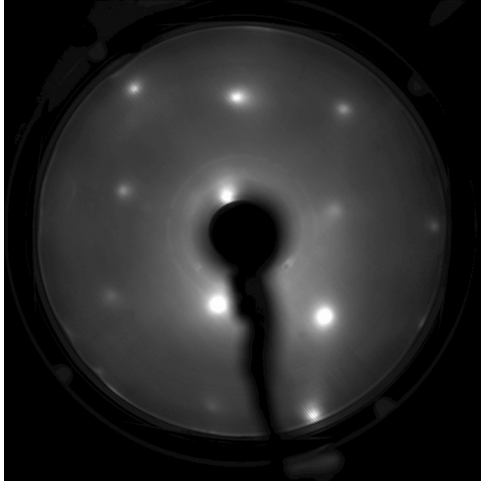
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FIG. 1. Low-energy electron diffraction patterns of Pd(100) ultrathin film with 4.6 nm thickness under the electron energy of 130 eV. The sharp (10) and (11) spots show that the sample is (100) oriented Pd film. These patterns do not disappear even after 1 h air adsorption.

to the (100) oriented Pd film with atomic flatness appeared after heating, where RHEED oscillation was not observed because of the complex process of this deposition method. The prepared samples were encapsulated in quartz tubes attached to the bottom of the preparation chamber to prevent gas adsorption [21]. In the low-energy electron diffraction images, fourfold symmetry spots in fcc (100) were confirmed even immediately after exposure of the film to air for 1 h (Fig. 1). The film thickness was evaluated by means of the quartz crystal microbalance during deposition and the x-ray refraction measurement after depositing. In addition, atomically flat step-and-terrace structures were confirmed in Pd films using an atomic force microscope. Without the three-step growth method, epitaxial Pd films cannot be obtained on an oxide substrate because of low oxygen affinities. We note that Pd film below 15 ML ($\sim$2.9 nm) cannot be epitaxially grown even with such a method. For these reasons, Pd(100) films with thicknesses of 2.9–10 nm were prepared. The magnetization

measurements were performed using a superconducting quantum interference device (SQUID) magnetometer and the XMCD experiments were carried out at beam line BL-14 at the HiSOR.

III. RESULT AND ANALYSIS

Figure 2(a) shows the nonlinear components of magnetization of Pd(100) films measured at 300 K, which demonstrates a saturation behavior below 5.55 nm. In a film with thickness of 10 nm, however, the nonlinear component was not observed as well as in the bulk Pd. Remanent magnetization and a coercive field of the film of 100–200 Oe were observed in the films having nonlinear magnetization curves [Fig. 2(b)]. Figure 2(a) also indicates the $\sim$10% decrease in the nonlinear component of magnetization after the Pd film had been exposed to air for a day.

The ferromagnetic nature found in the magnetic data in thicknesses below 5.55 nm was also confirmed by the XMCD spectra of Pd film that was exposed to air for a few minutes. As can be seen in the XMCD spectrum of 3.4 nm Pd thin film, which was obtained using the total electron yield method at room temperature under an applied field of 1.1 T perpendicular to the plane (Fig. 3), there are multiple XMCD peaks at the Pd M_3 edge near 532 eV, although no clear peaks were observed at the Pd M_2 edge. This behavior is not typical in conventional ferromagnetic materials, but it is essentially the same as the XMCD spectra of pure Pd nanoparticles showing ferromagnetic behavior [7,9]. This indicates that this ferromagnetic behavior originates in pure Pd instead of ferromagnetic contamination from Fe and so on. We note that additional peaks in x-ray absorption spectrum (XAS), due to the contribution from oxygen which is adsorbed on the surface of the Pd film and/or included in the STO substrate, are observed other than the white line at Pd M_3 edges (Fig. 3). This is because the oxygen K edge is very close to the Pd M_3 edge. Because the present measurements were performed using the electron yield method, we could not separate the intrinsic XAS signal of Pd from the background of the substrate, and thus it is difficult to estimate the amount of magnetic moment of Pd using the sum rule. In addition, no XMCD spectra are
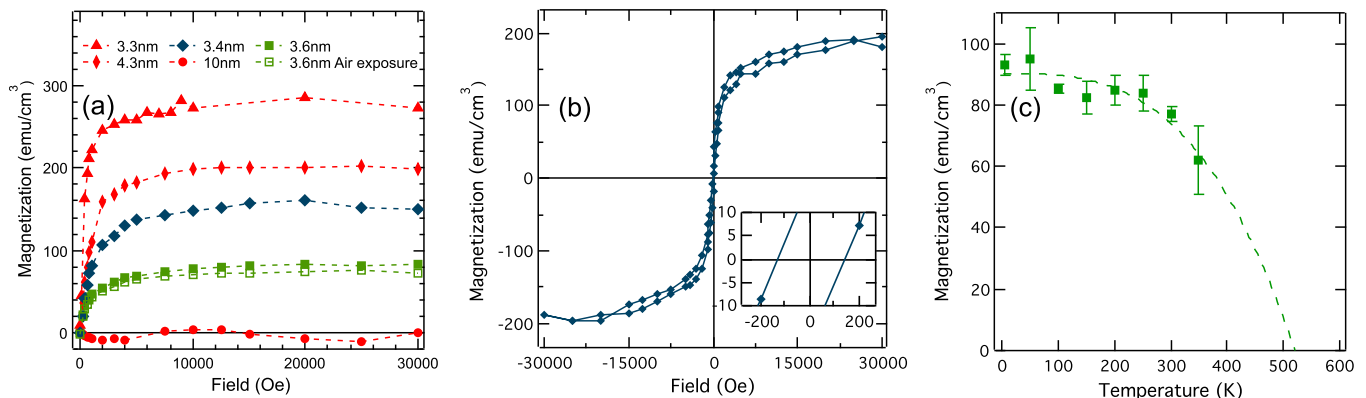

FIG. 2. (Color online) Results of magnetic measurements. (a) The extracted nonlinear components of magnetization of Pd(100) films measured at 300 K. After air exposure, the saturation magnetization is reduced 10%. 10-nm-thick Pd(100) thin film shows no nonlinear component. (b) The nonlinear magnetization curves of 3.4-nm-thick film. The inset shows the coercive field of the film of 100–200 Oe. (c) Temperature-dependent magnetization of 3.6-nm-thick film. The fitting is performed based on Bloch law for ferromagnets.
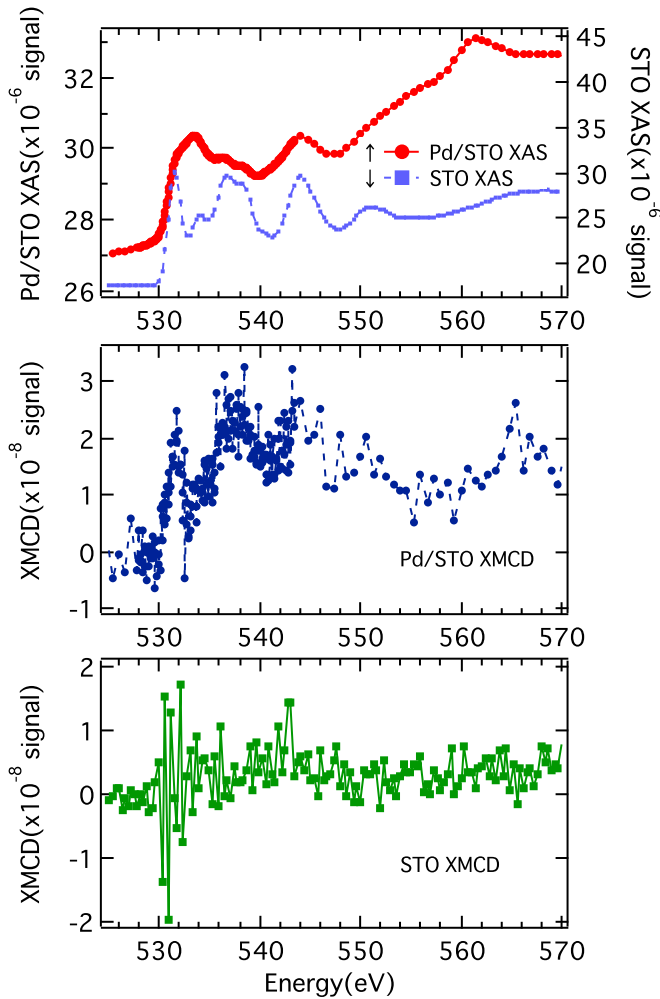
FIG. 3. (Color online) Result of XAS and XMCD measurement of Pd/STO and STO at room temperature. The multiple XMCD peaks are shown at the Pd M_3 edge near 532 eV, indicating that Pd(100) thin film appears to be intrinsically ferromagnetic. The peak shapes are similar to those of the ferromagnetic Pd particles [7,9]. In addition, there is no XMCD signal in STO substrate.

observed in STO substrate. Thus, the XMCD signal near the M_3 edge in Pd/STO originates from Pd. Therefore, we judged the ferromagnetism of Pd thin film to be intrinsic although the signal-to-noise ratio is not sufficient.

The magnetic moment per Pd atom, obtained from the spontaneous magnetization at 300 K, is plotted as a function of film thickness in Fig. 4. The oscillatory change in magnetic moment, having the period of ~ 1 nm corresponding to $5-6$ monolayers (ML), is clearly demonstrated in the range of 0.04–$0.61 \mu_B$/atom, where the magnetic moment of Pd film at 300 K is typically 20% smaller than that at 0 K, and the estimated Curie temperature is much higher than 500 K, as shown in Fig. 2(c). In other words, the magnetic moment and Curie temperature of the Pd film are comparable to those of Ni. The magnetizations increase off of a fitting curve below 100 K in Fig. 2(c). This behavior can be attributed to the structural phase transition of the substrate, because STO has a phase transition temperature at 105 K [22]. Thus, we pay attention to the magnetic data at 300 K and above, and not
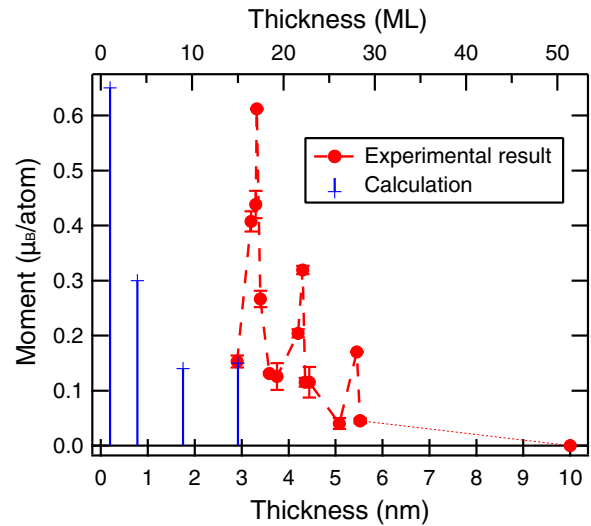

FIG. 4. (Color online) Thickness-dependent magnetic moment per Pd atom, which is obtained from saturation magnetization at 300 K. The overall error includes errors in the magnetic measurements using the SQUID magnetometer and the evaluation of magnetization. The oscillatory period of magnetic moment is ~ 1 nm corresponding to thick (5–6 ML). This is consistent with the predictions based on calculation [16].

to low-temperature data in the film-thickness dependence data in order to avoid the contribution from the phase transition of STO.

The appearance of spontaneous magnetization in Pd(100) in an oscillatory manner dependent upon film thickness has been predicted using first-principles computational techniques. The calculation by full-potential linearized augmented plane-wave method pointed out that the appearance of ferromagnetic moment is triggered by QW states in freestanding Pd films with 4, 9, and 15 ML [16]. The oscillatory change in magnetism with the period of 5–6 ML is in good agreement with the present results.

From the standpoint of the Eq. (1), I values of 0.41 [16] and 0.34 eV [23] have been reported for Pd, and thus the critical values of $D(\epsilon_F)$ for ferromagnetism are estimated to be 2.45 eV^{-1} atom^{-1} and 2.9 eV^{-1} atom^{-1}, respectively. $D(\epsilon_F)$ of 2.30 eV^{-1} atom^{-1} for bulk Pd is slightly small to satisfy Eq. (1). Therefore, it is predicted that Pd can change to a ferromagnetic metal by varying the $D(\epsilon_F)$ with the reduction of its dimension. In 4 ML (100) Pd film, for which ferromagnetism was predicted, $D(\epsilon_F)$ of 2.62 eV^{-1} atom^{-1} for the center layer [16], and an average value of $D(\epsilon_F)$ of 2.7 eV^{-1} atom^{-1} were evaluated to intrinsically satisfy Eq. (1) [18]. In addition, Hong *et al.* showed that the same condition is also satisfied in 9 and 15 ML (100) Pd films [16]. In this experiment, we were able to estimate that $D(\epsilon_F)$ of ~ 17 and ~ 22 ML (100) Pd films increases to satisfy Eq. (1).

The ferromagnetism due to QW states in the Pd film can be interpreted based on the electronic structure of bulk Pd. The h_5 band of Pd, which mainly contributes the DOS around Fermi energy, forms the Fermi surface. It has a jungle-gym-like structure along the $\langle 100 \rangle$ direction with the Fermi wave number

$k_F = 0.83$ in units of $2\pi/a$, where a is the lattice constant of Pd [24]. In the Pd film, only discrete wave number k_z is allowed along the [001] direction. The state of k_z is described in the phase shift quantization rule [25],

$$2\pi k_z N + (\varphi_s + \varphi_i) = 2\pi j, \qquad (2)$$

where N is number of layers, $\varphi_{s,i}$ is a correction term for the scattering phase shift at the surface and interface, and j is an integer quantum number. If $\Phi = -(\varphi_s + \varphi_i)/2\pi$, then

$$k_z = (j + \Phi)/N \qquad (3)$$

in units of $2\pi/a$. Thus, the value of N to satisfy the condition that the QW states cross ϵ_F at which ferromagnetism is expected through the Stoner criterion, appears with a period of $1/(1 - k_F) = 5.97$ ML for $k_F > 1/2$, which is independent of Φ [16,25,26]. The agreement with the first-principles calculation for Pd films points to a ferromagnetic origin based on QW states confined between the surface and interface.

This also explains why $N \sim 17$ ML (3.3 nm) for the first peak in experimentally obtained magnetic moment is slightly different from the prediction $N = 15$ ML (2.9 nm) in the calculation. The Pd film is deposited on an STO substrate, and thus Φ is not necessarily equal to the calculated value under the freestanding condition. From Eq. (3), the change in Φ results in the change in k_z and thus the shift of N for the crossing of QW states and ϵ_F. Recently, the difference of phase shifts of QW state in $SrVO_3$ (SVO) film at the vacuum surface and the STO interface was experimentally observed from angle-resolved photoemission spectroscopy (ARPES) measurement [27]. The absolute value of phase shift at the STO interface at ϵ_F is greater by 0.5π than that of the vacuum surface. We estimate the difference of the phase shifts $\Delta\Phi$ by subtracting Φ for $N = 15$ from that for $N = 17$ as 0.34 and -0.66 under the differences of the quantum number: $\Delta j = 0$ and 1, respectively. These correspond to $\varphi_i - \varphi_s = 0.68\pi$ and 1.32π. The value of $\varphi_i - \varphi_s$ of the SVO system ($\varphi_i - \varphi_s \sim 0.5\pi$ at ϵ_F) is located between the present evaluated values for $\Delta j = 0$ and 1. Thus, we did not come to evaluate the value of $\varphi_i - \varphi_s$ unless the ARPES measurement is performed. Nevertheless, it is reasonable to interpret the difference of the peak position in terms of the difference of the phase shift, because the evaluated value of $\varphi_i - \varphi_s$ is comparable to that of SVO system. In addition, the calculation showed that the spin density due to the polarized $4d$ bands was spread over the entire thin film [18]. This is consistent with the observation that the magnetic moment of Pd film was reduced but remained considerable even after exposure to air, because the adsorption of oxygen can significantly modify the magnetic moment of Pd near the film surface through the charge transfer.

It is necessary to mention that some ambiguity remains in the comparison of experimental data with the theoretical prediction about QW states. First, strain slightly presents in the Pd film on STO substrate. We recently detect slight lattice expansion due to the lattice mismatch with 0.4% between Pd and STO by means of the surface x-ray diffraction technique using synchrotron radiation [28]. Such a distortion in the films may explain the discrepancy of the amplitude of magnetic moment of Pd atom between the experimental data and the calculation. The detailed discussion based on the energy band calculation is necessary. In addition, we should pay attention to the presence of two-dimensional electron gases on the surface of STO [29]. This can cause the modification of interface to change the phase shift and thus the film thickness dependence of magnetization. Nevertheless, we believe that a QW mechanism is appropriate to explain the oscillatory magnetization depending on the film thickness in the Pd(100)/STO system.

That ferromagnetism appears only in (100) facets of Pd nanoparticles [3] is consistent with the notion that ferromagnetic origin is based on the QW states. This is because the jungle-gym-like structure of the Fermi surface along the $\langle 100 \rangle$ direction is essential to the appearance of ferromagnetism in Pd through the Stoner criterion. Thus, it is difficult for (111) or (110) Pd film to become ferromagnetic.

IV. CONCLUSION

Our experiment systematically demonstrates the appearance of ferromagnetism in nonmagnetic metal in bulk according to the Stoner criterion using the QW states formed in a nanosized structure. The observed magnetic behavior is qualitatively supported by the first-principles calculation. The present result opens the way to systematically tuning a desired magnetic state by changing film thickness and/or adjusting the scattering phase shift at the interface. A calculation published in a recent study showed that the application of an electric field to achieve a surface carrier density of $>10^{13}$ cm^{-2} can induce the magnetic transition in (100)Pd film [18], where the condition can be realized using an electric double layer. It is further expected that a reduction of the applied electric field could be achieved by adjusting the conditions to the boundary of magnetic transition. These findings can be used to realize innovative developments in terms of magnetic control of metallic materials using external fields.

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