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# Sharply distinct *d*-band quantum-well states in palladium thin films

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We probe *d*-band quantum-well (QW) states in Pd nanofilms grown on Cu(001) using first- principles density functional theory (DFT) calculations combined with scanning tunneling spectroscopy (STS) experiments. This study reveals that QW states occur in the Pd overlayer films over a strikingly large film thickness and in a large binding energy range. The magnetic quantum number resolved orbital characters of these states are identified unambiguously by our DFT calculations. Calculations also demonstrate oscillatory multilayer relaxation and *d*-derived quantum size oscillation of the electronic density of states at the Fermi energy. The pseudomorphic growth, well-defined interface, and STS with single-layer thickness resolution allow us to probe individual QW states arising from the electron confinement along the growth axis of Pd films and to extract an accurate dispersion of the ($\Delta_5$-type) *d* electronic band, as these states are laterally highly localized and give rise to distinct and sharp peaks in the tunneling spectra.

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Electron confinement in thin metal films is an extremely fascinating topic of both theoretical and applied research, as it addresses the fundamental issues described in quantum mechanics textbooks and simultaneously holds a promise of engineering films with desired device properties [1–6]. As the film thickness is reduced to the range of the de Broglie wavelength ($\lambda_d$) of electrons, quantum size (QS) effects become important—manifesting themselves through the oscillatory thickness dependence of film properties. The oscillations of these properties with the film thickness are determined mainly by singularities in the density of states (DOS) at the Fermi level ($E_F$), which are caused by the restriction of electron motion within the film. In such films, the electrons moving along the direction perpendicular to the film surface become quantized into the well-known quantum-well (QW) states [1].

The resulting two-dimensional (2D) electronic structures have been studied intensively in the past, mostly by lateral averaging techniques such as photoemission spectroscopy (PES) and inverse photoemission spectroscopy (IPES) that probe the occupied and unoccupied electronic states, respectively [7–9]. Since these techniques use lateral averaging, they require highly homogeneous films with a constant thickness over the sample area of 0.1 mm. Only a few systems can be prepared with such a high uniformity.

A complementary approach is opened by scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS), with a spatial resolution on the atomic scale, where the information is not averaged over the structural variation and which can probe both the occupied and unoccupied states depending on the polarity of the tip/sample bias voltage. Making use of this approach, there are a few studies [10–14] where the QW states in a noble metal are derived from the nearly free-electron-like *sp* states, while studies of the *d*-derived QW states are extremely rare, even though the latter are known to be extremely important for magnetic coupling effects in transition metal film structures and particularly for magnetocrystalline anisotropy oscillations in ferromagnetic films [3,15,16].

A study of *d*-derived QW states is much more challenging than that of *sp* QW states due to the large number of states which crowd the *d* manifold and are localized in a narrow energy range [3,4]. Since *d* electrons have much more localized wave functions near the atomic core and decay faster in the vacuum region, only at closer tunneling distances could the STM and STS be sensitive to the electronic *d* bands, but then, the tip-sample interaction may introduce modifications in the electronic structure of the tip and sample.

In view of such limitations and challenges, in this Rapid Communication, we investigate the electronic structure of thin atomically flat Pd films on a Cu(001) substrate using STS with a single-layer thickness resolution. Pd is of particular interest because its *d* bands cross the $E_F$ and are broader than those usually found for Ag or Cu. Owing to its broader 4*d* bands, we observe that QW states occur in the films of Pd over a strikingly larger film thickness [up to 17 monolayers (ML)] and in a larger binding energy range (from about −3 to 0 eV), contrary to popular belief. Examining the orbital characters of the electronic band structures, it is identified that, in Pd thin films over Cu(001), only *d* electrons can form QW states for this energy range. The central issues of the present study are as follows: with varying thickness how the changes in the quantum size (QS) effects, including QW states, occur, how the STS technique can be effectively applied to succeed in observing the *d*-derived QW states, and, by probing individual QW states and determining their energetics, how an accurate dispersion of the ($\Delta_5$-type) *d* electronic band can be extracted. Our first-principles calculations in the framework of density functional theory (DFT) [17] account for the explanation of the observed effects and provide us useful information on *d*-derived QS effects.

Pd is a divalent late transition metal with a filled 4*d* shell crystallizing in the fcc structure which has a large density

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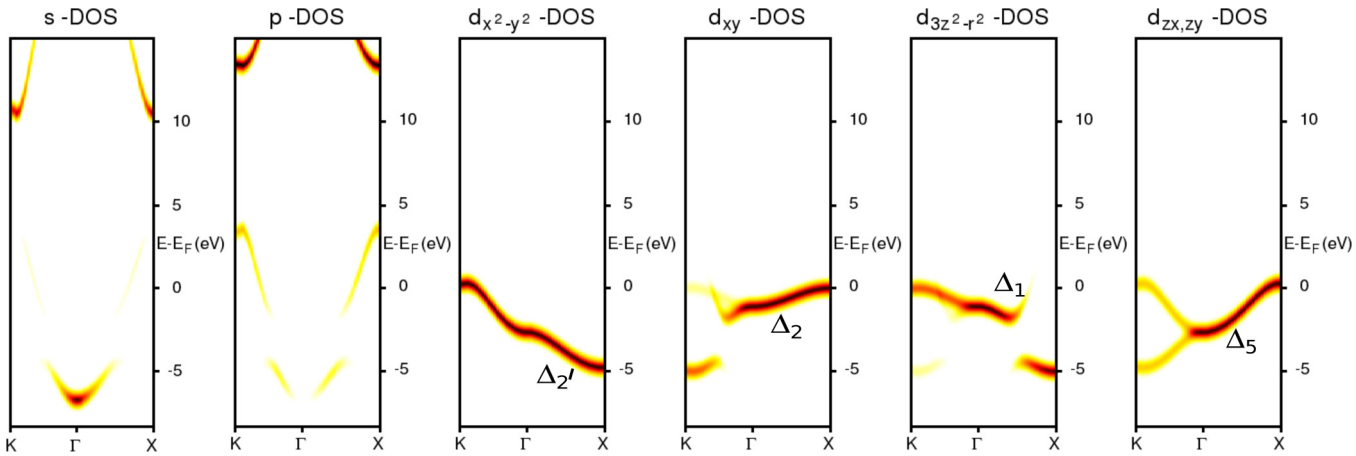


FIG. 1. (Color online) Orbital selective $k$-resolved electronic density of states (EDOS) of bulk Pd. The $\Delta_5$ band mostly has a $d_{zx,zy}$-orbital character responsible for our observed QW states. The color scale yellow (light) and red (dark) correspond low and high EDOS, respectively.

of states near its Fermi level. For Pd, the bottom of the $s$-type valence band is situated below the binding energy of $-5$ eV and the top of the $sp$ band above $E_F$, leaving the energy range of 0–3 eV below $E_F$ (where the QW states are observed in our experiment) for the bands with a strong $d$-type character (see Fig. 1). In this energy window, the band structures along the $\Gamma$-$X$ (001) direction mainly consist of two bands: a fairly dispersive $\Delta_5$ band originating mostly from $d_{zx}$ and $d_{zy}$ states, and an almost flat $\Delta_2$ band derived from $d_{xy}$ states. When the Pd film becomes sufficiently thin along the $z$ direction to realize the quantum confinement of Pd-4$d$ electrons in the film, the bands originating from the $d_{zx}$ and $d_{zy}$ states are expected to form quantized states because these orbitals extend along the $z$ direction, whereas the $d_{xy}$ state remains almost unchanged because of its 2D character in the $xy$ plane. Along the $\Gamma$-$X$ (001) direction, the $d_{x^2-y^2}$ orbital has a contribution below the binding energy of $-3$ eV (out of our experimentally probed energy window); in contrast, the $d_{3z^2-r^2}$-derived band falls within our observed energy range but does not extend fully over the whole $\Gamma$-$X$ (001) Brillouin-zone line. For our experimentally relevant energy range and Brillouin-zone window, only $d_{zx}$ and $d_{zy}$ orbitals are highly significant.

The $N$ monolayers (ML) of Pd films grown on the Cu(001) substrate [Pd($N$ ML)/Cu(001)] are simulated by using supercell geometry with a vacuum of more than 10 Å in the $z$ direction to ensure a negligible interaction between its periodic images. The Cu(001) substrate is approximated by a four-layer slab with the interlayer distances of the three bottom-most layers keeping fixed in its bulk Perdew-Burke-Ernzerhof (PBE)-optimized value of 1.817 Å. Except for these three bottom layers, the rest of the whole system including the Pd overlayers are fully relaxed so as to minimize the forces acting on the atoms using a conjugate-gradient algorithm. The corresponding Pd(9 ML)/Cu(001) structure is rendered in Fig. 2(a). Pd(001) has a primitive square net with an in-plane lattice spacing of 2.795 Å (PBE value), which does not match that of Cu(001) (2.570 Å). This large in-plane lattice mismatch (about 8.2%) induces a large compressive strain in the Pd overlayer on Cu(100). The strain as well as the presence of dissimilar neighbors as found at the interface and the absence of some out-of-plane neighbors (due to termination of the solid) as found at the surface lead to sizable structural relaxations. For this Pd(9 ML)/Cu(001) system, the interlayer relaxation between the overlayers $i$ and $i+1$, $\Delta d_{i,i+1}$, is defined as (given in percent) $\Delta d_{i,i+1} = 100\frac{(d_{i,i+1}-d_a)}{d_a}$, where $d_{i,i+1}$ is the interlayer distance between two adjacent layers parallel to the substrate and $d_a = 2.013\,35$ Å is the average of the two most converged interlayer distances in the interior of the Pd film. As shown in Fig. 2(a), $i = 1$ and $i = 9$ correspond to the interface and surface Pd layer, respectively. The signs $+$ and $-$ of $\Delta d_{i,i+1}$ indicate the expansion and contraction of the interlayer spacings, respectively. For the two topmost surface layers, the value of $\Delta d_{8,9}$ is $-0.8\%$. Moreover, we find that the relative interlayer spacings oscillate as a function of the thickness of the film with a damped amplitude [see Fig. 2(b)], clearly indicating the QS effect in the interlayer relaxation [22,23]. We also calculate the projected EDOS at $E_F$ for Pd atoms located at different overlayers of the Pd(001) film. The

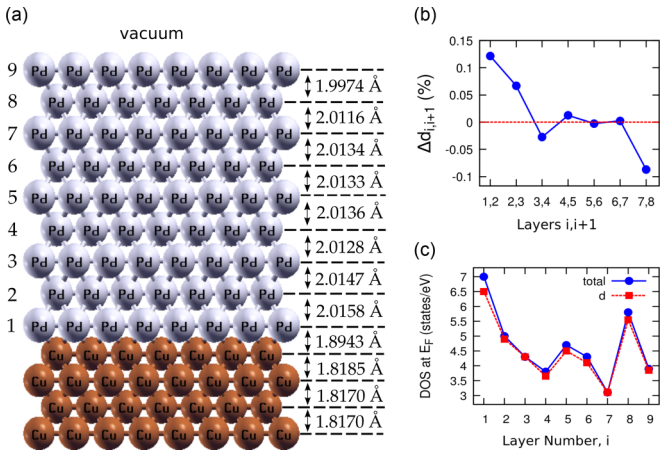


FIG. 2. (Color online) (a) Pictorial side view of the calculated structure for 9 ML of Pd on a Cu(001) substrate. Our structure optimization, which allows selective dynamics along the $z$ axis, exhibits multilayer relaxation. (b) Multilayer relaxation as a function of the respective interlayer, going from the interface (left) to the surface (right). (c) Electronic DOS at $E_F$ as a function of overlayer thickness, exhibiting QS oscillations.

results are plotted in Fig. 2(c), which shows an oscillation in EDOS. The EDOS at $E_F$ are mainly contributed from the 4$d$ states of Pd atoms, which indicates that the characteristic of the EDOS oscillation of the Pd film is mostly dominated by the 4$d$ electrons while $s$ and $p$ electrons play a negligible role. These findings suggest that the QS effect can also be important for a thin $d$-band metal film, contrary to the common belief that the QS effect should be smeared out in the transition metals as their Fermi wavelengths are highly anisotropic. Pd is indeed exceptional as it has dispersive and broad 4$d$ bands which cross its Fermi level. Usually, $d$ electrons are expected to be bound to the ion site and move in the crystal structure by hopping from one site to a neighboring site. However, in Pd, the intraorbital hopping term for $zx$ and $zy$ orbitals that expand in the $z$ direction is quite large, and hence, the resulting $\Delta_5$ band of Pd exhibits a large dispersion, shifting in energy about 3 eV when moving in the Brillouin zone from the center to the edge (see the last panel of Fig. 1). A more detailed analysis of EDOS for Pd(9 ML)/Cu(001) reveals that the EDOS at $E_F$ are mostly contributed from $d_{zx}$, $d_{zy}$, and $d_{xy}$ orbitals while $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ play a minor role. The $d_{xy}$ orbital has the largest contribution at $E_F$, but its EDOS peak is highly localized near $E_F$ and no significant peak is observed in the energy range of 0.5–3 eV below $E_F$, where the QW states are observed in our experiment. In this energy window, the $d_{zx}$ and $d_{zy}$ orbitals are highly significant. Our layer-resolved STS experiment allows us to probe individual QW states and extract the dispersion of the $d$ electronic band of $\Delta_5$ type.

The experiments were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure below $2 \times 10^{-11}$ mbar during Pd deposition in order to avoid unwanted contamination. To resolve the many possible $d$ states in a film, it is important to eliminate extrinsic peak broadening. The most common problem is film roughness. In our work, we employed atomically uniform films of Pd grown on Cu(001) by molecular beam epitaxy (MBE). For STM, we used chemically etched polycrystalline W tips, followed by flashing the tip to 2200 K. The differential conductivity $\frac{dI}{dV}$ was measured in STS mode using a lock-in technique with a typical modulation frequency of 3.6 kHz and a modulation voltage ($V_{rms}$) between 10 and 15 mV. The spectra were taken in both directions, from higher to lower and from lower to higher sample bias, in order to correct the binding energy shift due to the finite time constant. A single crystal of Cu (001) was cleaned by a repeated cycle of $Ar^+$ sputtering and subsequent annealing at 900 K until clean Auger electron spectroscopy (AES) spectra, sharp low energy electron diffraction (LEED) spots, and atomically smooth terraces under STM were observed. Pd films were evaporated from an electron beam evaporator with a deposition rate of 0.5 ML/min at room temperature. During deposition the growth process was monitored by reflection high energy electron diffraction (RHEED). During STM/STS

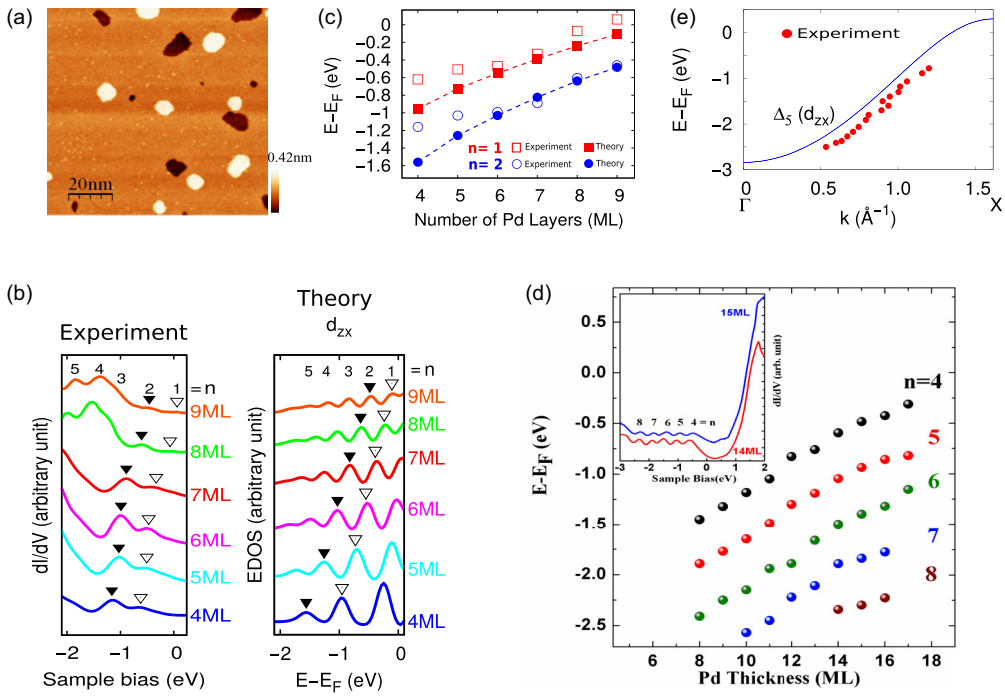


FIG. 3. (Color online) (a) Large scale (100 nm × 100 nm) STM topography image of the Pd/Cu(001) sample with a nominal thickness of 6 ML. This typifies the surface morphology of all the films discussed in this Rapid Communication, confirming almost perfectly layer by layer growth of Pd on Cu(001). The sample bias voltage ($V_s$) and tunneling current ($I_t$) were 0.4 V and 1 nA, respectively. (b) The tunneling spectra ($\frac{dI}{dV}$), acquired on the flat films with various local thicknesses represented by the number of monolayers, are compared with our theoretically calculated $d_{zx}$-orbital density of states at the Brillouin-zone center. Prior to spectroscopy, the tunneling gap was set at 4 nA and 0.5 V. The successive spectra are graphically offset for clarity. (c) QW peak energy of $\frac{dI}{dV}$ spectra (experiment) and density of states (theory) in (b) as a function of the number of Pd overlayers. (d) QW peak energy of $\frac{dI}{dV}$ spectra (as in the inset where the spectra for 14 ML and 15 ML are shown as examples) with the number of Pd overlayers. (e) Energy dispersion of the Pd band along the Γ-$X$ direction as determined from the thickness dependence of the QW energy.

measurements, the sample was kept at 4.7 K, and the energy resolution was 1.2 meV, corresponding to $3.5k_BT$. Note that we took exceptional care to avoid tip-induced artifacts in the spectra by acquiring a very large database. In the present work, we focus only on the reproducible features in the spectra.

A large scale (100 nm × 100 nm) topographic image of the Pd/Cu(001) system measured in a constant current mode with a 0.4 V tip bias and 1 nA tunneling current is shown in Fig. 3(a) for the Pd films with a nominal thickness of 6 ML, which typifies the surface morphology of all the films discussed in this Rapid Communication. The film is atomically flat, with terraces several hundreds of angstrom wide. The pseudomorphic growth and well-defined interface make it an ideal candidate to study QW states by STS. We found that when the Pd thickness was smaller than 18 ML, only stable layer by layer films were obtained and the films thinner than 4 ML tended to be rough.

Figure 3(b) shows the tunneling spectra ($\frac{dI}{dV}$) measured on a variety of Pd films of different thicknesses in the energy range of about 0–2 eV below $E_F$. Note that we determine the thickness of the film on which we obtained the particular spectra by measuring the spectra not only on a variety of different Pd films with varying thicknesses, but also by taking the advantage of real-space resolution, and acquiring spectra on individual terraces separated by monatomic layer high steps. Measuring the spectra for each individual thickness for different samples, we directly correlate the tunneling spectra and the film thickness.

Each of the spectra consists of a series of peaks that reflect the formation of QW states. With increasing film thickness, the energy of each QW increases towards $E_F$, which is in accord with our DFT calculations [see Fig. 3(b), right panel]. For 7 and 8 ML films of Pd, at higher energy (above $n = 2$) there is a sharp jump in the tunneling conductance, which can be attributed to the onset of possible surface resonance states below $E_F$. For a direct comparison, the peak energy of the $\frac{dI}{dV}$ spectra (experiment) and EDOS (theory) as a function of the number of Pd overlayers are plotted in Fig. 3(c), which show a reasonable agreement. Furthermore, it is interesting to see how many monolayers are necessary for the $n + 1$ QW state (for example, $n + 1 = 2$) to arrive $E_F$ after the $n$ QW state (for example, $n = 1$) reaches there. By extrapolating the curves in Fig. 3(c), we find that it is about 3 ML, i.e., $t(n + 1) - t(n) \approx 3$ ML, where $t(m)$ denotes the thickness at which the $m$ QW state reaches $E_F$. This theoretical value agrees with the experimental one, and also is very close to the value obtained from a previous prediction [24], which suggests $\frac{1}{2(k_{ZB}-k_F)} = 2.976$ ML for the (100) orientation where $k_{ZB}$ is the lattice periodicity (=1.0) and $k_F$ is the Fermi wave vector (=0.832 for Pd [25]).

In our experiment, we go further with the number of Pd layers and more peaks keep on appearing [see the inset of Fig. 3(d), where the $\frac{dI}{dV}$ spectra for a couple of monolayers are shown as an example]. For rather thick films (more than 17 ML) a continuous band forms (not shown in the figure). STS can probe both the occupied and unoccupied states. The unoccupied QW states are not observed in our experiment [see the inset of Fig. 3(d)] because there is no $\Delta_5$ band +0.3 eV way above the Fermi level of Pd. The high intense peak as shown in Fig. 3(d) at around 1 eV above $E_F$ can be interpreted as an associated surface resonance state coming from Pd(001). This surface state energy is almost independent of the Pd film thickness, i.e., the state lacks dispersion. This observation is in agreement with the inverse photoemission study in Pd(001) [26]. Since the STS is very surface sensitive, the intensity of the unoccupied surface resonance state is much larger than the more localized occupied QW states. The dependence of energies $E$ of the observed QW states on film thickness [shown in Fig. 3(d)] allows us to derive the band dispersion along the $\Gamma$-$X$ direction. The QW state energies for the eigenmodes from $n = 4$ to 8 are obtained for film thicknesses between 8 and 17 ML, and the dispersion of the corresponding bulk band is derived by using the phase accumulation model [27],

$$2k_\perp d + \Phi = 2\pi n, \tag{1}$$

where $k_\perp$ stands for the $k$ value perpendicular to the film plane, $d$ for the film thickness, $\Phi$ for the total phase change due to the reflection at the two boundaries, and $n$ for the number of QW states. In order to calculate $k_\perp$ with Eq. (1), the experimental data points are interpolated. A number of thicknesses are used to determine $k_\perp(E)$ via a least-squares fitting procedure and calculating $\Phi(E)$ from the phase accumulation model (as detailed in Refs. [2,3,27]). The analysis then leads to the band dispersion which is shown in Fig. 3(e). For a direct comparison, our DFT-calculated dispersion of the $\Delta_5$ band for bulk Pd is plotted with a solid line. The experimentally derived dispersion is consistent with the theoretical one. Most importantly, the uncertainty of $\Delta k_\perp$ remains quite narrow since the thickness fluctuation of our system is very small.

In conclusion, we use combined first-principles DFT calculation and STS experiment to investigate $d$-band QW states in Pd nanofilms grown on Cu(001). This study reveals that $d$-band QW states occur in the Pd overlayer films over a strikingly large film thickness and in a large binding energy range. The pseudomorphic growth, well-defined interface, and atomically resolved STS allow us to probe individual QW states originating from the electron confinement along the growth axis of Pd films and to extract the accurate dispersion of the ($\Delta_5$-type) $d$ electronic band. Our DFT calculations account for the explanation of the observed effects and provide further information regarding $d$-derived QS effects such as oscillations in multilayer relaxations and in EDOS at $E_F$. These theoretical understandings and experimental controls are likely to incite futuristic device applications based on the exciting ability to control the confinement properties through wave-function engineering of electronic structures at the nanoscale. In this respect, the present work deepens and extends the subject of QW states, in general.

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