# Kondo effect of single Co atoms adsorbed on Pb/Si(111) nanoislands

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Using scanning tunneling spectroscopy, we have investigated the local electronic property change upon single Co atom adsorption on Pb nanoislands and/or films grown on a Si(111)-7×7 surface. The quantum well states formed on the clean Pb film were found to be locally destroyed by the adsorbed single Co atom. Moreover, the differential conductance $dI/dV$ curves, exhibiting an asymmetric line shape with a dip and a hump, respectively, below and above the Fermi level, demonstrated a Kondo effect from the adsorbed Co atom on the Pb film. The similar line shapes of the $dI/dV$ spectra and the similar Kondo temperatures for Co atoms adsorbed on Pb island areas of different Pb thicknesses further showed that the different densities of states at the Fermi level originated from the quantum well states do not play a significant role, possibly due to the destruction of the quantum well states upon the Co atom adsorption.

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## I. INTRODUCTION

The nanostructures with a permanent magnetic moment may play a key role in future spinelectronic technologies.[1] Many of these systems can be described by the Kondo problem.[2] The first observation of Kondo effect is from the measurement of resistivity of nonmagnetic metal with a small amount of magnetic impurities, where the resistivity anomalously increases at temperatures lower than the so-called Kondo temperature ($T_K$). The explanation of Kondo effect involves the interaction between the magnetic impurities and the conduction electrons of the host metal. This interaction leads to a magnetic-moment screening effect by the spins of conduction electrons around the magnetic impurity and thus results in the anomalous resistivity at the temperatures lower than $T_K$.

The understanding of the physics in single magnetic atom adsorption on metallic surface is a fundamental basis to the possible applications of magnetic nanostructures. Combining the scanning tunneling microscopy (STM) and the scanning tunneling spectroscopy (STS), both the morphologic structure and the electronic structure can be probed for a single magnetic atom adsorbed on metal surfaces. The spectroscopic behavior of surface Kondo effect has been studied theoretically[2–4] and experimentally.[5–10] The experimental observations of the surface Kondo effect include Mn/Nb(110),[5] Co/Au(111),[6] Ce/Ag(111),[7] Mn/NiAl(110),[8] Co/Ag(111), and Co/Cu(111),[9,10] just to name a few examples. Since the Kondo effect involves the spin-flip processes of the conduction electrons of the surrounding host nonmagnetic metal, naturally, one might ask what kind of role the density of states (DOS) near the Fermi level ($E_F$) play in the Kondo effect.

Thin metallic films possessing quantum confinement effect can provide a way to tune the density of states near the Fermi level.[11] For example, Pb film grown on semiconductor substrate shows quantum well states (QWSs), resulted from the electron confinement in the direction perpendicular to the film.[11,12] In the presence of QWS, DOS at the Fermi level depends on the relative positions of QWSs from $E_F$, which is in turn determined by the thickness of the metal films. For Pb film or island, the increase in the film thickness leads to an oscillation of DOS at $E_F$, which has been demonstrated to induce an oscillation in the morphological structure, surface energy, thermal stability, and superconductivity.[13–21] A very recent work has demonstrated that the Kondo temperature of a single manganese phthalocyanine (MnPc) molecule adsorbed on Pb films oscillates with the thickness of the films.[22] So far, the Kondo effect of a single magnetic atom on thin Pb films with different thicknesses has not yet been reported.

In this paper, we report our findings on the electronic property changes induced by a single magnetic Co atom adsorbed on the atomic flat surface of a Pb nanoisland grown on Si(111)-7×7. The QWSs were observed on the bare Pb surface area but disappeared on the adsorbed single Co atoms. The differential conductance spectra taken over single Co atoms showed asymmetric line shapes near the Fermi level, indicating the effect of Kondo resonance. The Kondo resonances on Co atoms adsorbed on surface areas of different Pb film thicknesses exhibited negligible difference, in contrast to the significantly different DOSs at the Fermi level on the bare Pb terraces. This insensitivity to the DOS at the Fermi level is consistent with our observation of the suppression of QWSs. Both effects indicate a strong interaction between the Co atom and the Pb surface, rendering a separate consideration of the QWSs of the Pb film and a perturbative picture of Co adsorption invalid.

## II. EXPERIMENT

We used silicon wafer as the substrate. It was cut to a proper size followed by ultrasonic cleaning in water and acetone. After transfer into the ultrahigh vacuum, the wafer was first degassed at 600 K for 24 h. The clean Si(111)-7×7 surface was prepared by a standard procedure:[23] flashing it to 1520 K a number of times until the Si wafer could be held at 1520 K for 1 min under a pressure of $<1\times10^{-9}$ torr and cooling it quickly down to 1220 K and then slowly down to room temperature at a rate of 2 K/s.

 

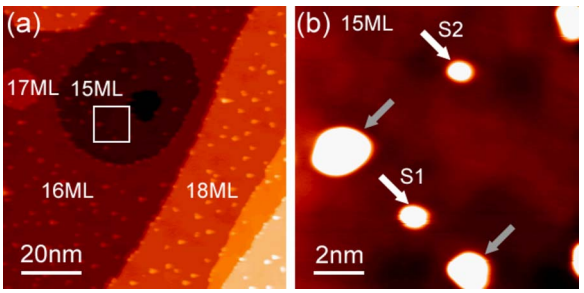


FIG. 1. (Color online) (a) A topographic STM image ($100\times100$ nm$^2$) of a Pb island with Co atoms deposited on it. The image is taken at a bias of +1 V and a tunnel current of 0.15 nA. (b) A close-up STM images ($15\times15$ nm$^2$) of the square area in (a), taken at +1 V and 0.15 nA. The sample temperature is 5 K.

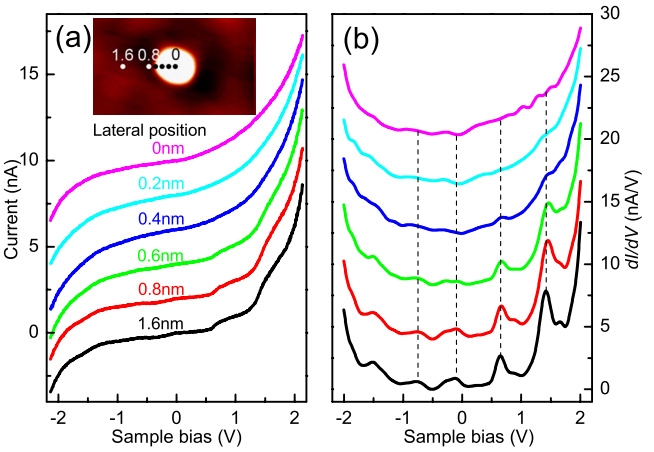


FIG. 2. (Color online) (a) The *I-V* spectra and (b) the corresponding differential conductance $dI/dV$ spectra at different positions along a line near an adsorbed Co atom on the Pb island surface. The tip height is set by a bias of +1.5 V and a tunnel current of 3 nA. The quantum well states appear as peaks in the $dI/dV$ spectra. As the STM tip moves toward the center of the Co atom, the quantum well peaks become vanished. The inset in (a) shows the positions at which the *I-V* curves are taken.

Pb was deposited onto the clean Si(111)-$7\times7$ surface at a rate of 0.01 monolayer (ML)/s from an electron-beam evaporator. The Pb source was placed in a molybdenum crucible ~20 cm away from the substrate surface and was thoroughly degassed before deposition. The Si(111)-$7\times7$ substrate was kept at 170 K during deposition and the as-grown sample was annealed at room temperature for 1 h. The formed Pb islands usually had a flat top or had a volcano-shaped top with a central hole surrounded by terraces. The latter kind of island could already provide a Pb film with a various thickness that is suitable for the thickness dependence studies. On top of the Pb island, Co atoms were evaporated from an electron-beam evaporator with a short Co rod as the source. Here, the sample was kept at room temperature without further annealing.

The measurements were carried out in the Omicron low-temperature STM operated in ultrahigh vacuum with a base pressure of $7\times10^{-11}$ torr. The STM tip was a chemically etched Pt/Ir tip, which, prior to its first use, was cleaned by $Ar^+$ sputtering. All the measurements were performed at a temperature of 5 K. We used the STM imaging mode to characterize the morphology of the sample surface and the STS mode of current ($I$) versus bias voltage ($V$) spectroscopy to measure the local electronic property. The differential conductance $dI/dV$ curves were numerically obtained from the tunneling *I-V* spectra, which were smoothed using fast Fourier transformation method to filter out the high-frequency noise first. This smoothing procedure may lead to a broadening by about 15% in energy width for the relevant features reported in this paper.

## III. RESULTS AND DISCUSSION

Figure 1(a) shows a $100\times100$ nm$^2$ STM topographic image of a Pb island deposited with Co atoms. Because of the volcano-shaped top surface, this Pb island consists of terraces with a height ranging from 14 to 20 ML with respect to the Pb wetting layer. The height difference between two adjacent terraces is of 1 or 2 ML. Before the Co atoms are deposited, the surface of the terrace is atomically flat with a corrugation smaller than 0.05 nm. As shown in the large area STM image and in the close-up STM image in Fig. 1(b), the deposited Co atoms appear as small protrusions with typical lateral sizes from 1 to 3 nm and typical heights from 0.2 to 0.4 nm. At this coverage, the adsorbed Co atoms can stay in single atom or small cluster form. Here, we regard the smallest protrusion features among all the adsorption structures as the single Co atoms. As labeled by S1 and S2 with white arrows in Fig. 1(b), these protrusions are quite circular in shape with a height of 0.2 nm, comparable with the diameter of a Co atom. The round boundary of these features, in contrast to that of the larger protrusions labeled by gray arrows in Fig. 1(b), further supports the assignment of S1 and S2 to be single Co atoms. Due to the tip size convolution, the lateral size of such features is on the order of 1 nm, larger than a single atom but comparable with the STM image size of a single Mn atom adsorbed on single-crystal Nb substrate[5] in a different system. In this paper, we focus on the investigation of the electronic properties of single Co atom adsorption on Pb islands and will not discuss the results on Co clusters.

We have measured a series of *I-V* spectra at different lateral positions along a line with respect to a Co atom (S1) for energies ranging from −2 to +2 eV. The corresponding *I-V* spectra and numerically differentiated $dI/dV$ curves are shown in Figs. 2(a) and 2(b), respectively, where vertically shifts are made for clarity. The inset in Fig. 2(a) shows the positions at which the spectra were taken with respect to the center of protrusion S1. The set of peaks in the $dI/dV$ spectrum on bare Pb surface [the bottom curve in Fig. 2(b)] is due to the QWSs formed in the Pb thin films.[11,12] The positions of the QWS peaks are indicated by the vertical dashed lines. These QWS peaks remain intact at the edge of the protrusion (labeled 0.8 nm) and start to diminish monotonically when the STM tip continues to move toward the center of the protrusion. At around 0.2 nm away from the protrusion center, all the QWS peaks are practically vanished with no signature of the quantum well states remaining.

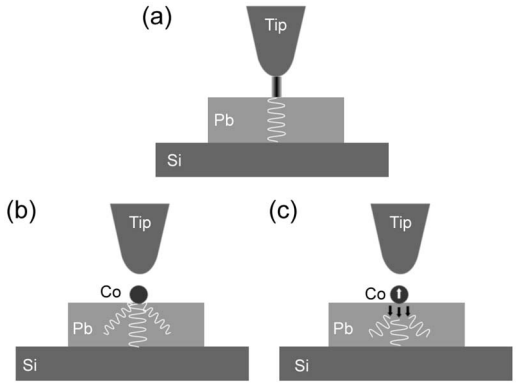


FIG. 3. (a) A sketch showing the quantum well states in the Pb island and the detection by an STM tip. (b) A sketch showing the scattering of the quantum well state electrons by an atom with weak interaction. (c) A sketch showing the Kondo effect, namely, the conduction electron cloud near a magnetic impurity, forms a shell structure with opposite spin orientation in the adjacent regions. A strong interaction destroys the quantum well states.

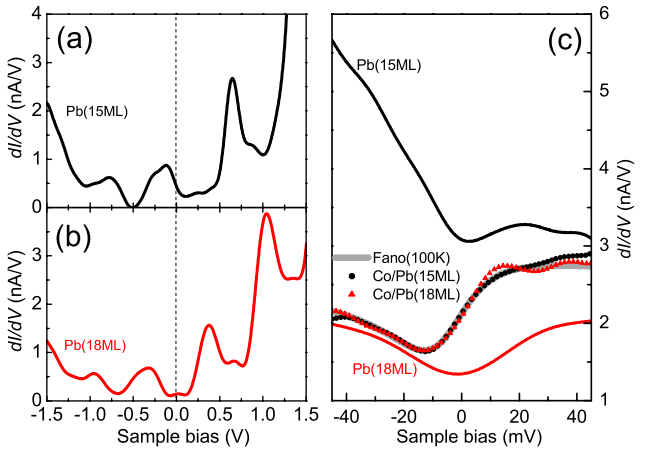


FIG. 4. (Color online) (a) The differential conductance $dI/dV$ spectra on a terrace of 15 ML Pb thickness. The tip height is set by a bias of +1.5 V and a tunnel current of 3 nA. (b) Similar to (a) but on a terrace of 18 ML Pb thickness. (c) The $dI/dV$ spectra in a smaller energy range on bare Pb terraces of 15 and 18 ML thick and on the single Co atoms adsorbed on terraces of 15 and 18 ML Pb thick. The tip height is set by a bias of 0.1 V and a tunnel current of 0.3 nA. A fitting line with Fano line shape to the $dI/dV$ spectra on Co atoms with a Kondo temperature $T_K \sim 100$ K is also shown in a thick gray line.

To understand the suppression of QWSs by a single Co atom, we have drawn schematics for the tunneling processes probed by an STM tip on bare Pb surface in Fig. 3(a) and on Co atom adsorbed on the Pb film in Figs. 3(b) and 3(c). In Fig. 3(a), the quantization of electronic wave in the perpendicular direction leads to a formation of electronic standing wave (corresponding to a QWS) inside the Pb island, similar to a standing light wave in a Fabry–Pérot optical interferometer. The tunneling current between the Pb film surface and the STM tip is determined by the probability of electrons tunneling through the classical forbidden vacuum area. In the case of Fig. 3(b), where the Co atom is assumed to weakly interact with the film surface, the quantization condition in the perpendicular direction remains intact inside the Pb island and the density of states of the QWSs remains unchanged. Due to the energy-level mismatch between the single Co atom and the Pb islands, the Co atom behaves like an atomic scattering center, reducing the electrons from QWSs to tunnel into the STM tip or the electrons to tunnel from the STM tip into the empty QWSs. In this case, the single Co atom just behaves like an attenuator to reduce the intensity of the tunneling current at all electronic energies including those of the QWS peaks. Indeed, such a behavior was found for MnPc molecule adsorbed on Pb films, as reported in Ref. 22. However, as judged from the $dI/dV$ curves in Fig. 2(b), in the tunneling spectrum on the Co atom, while an overall smooth varying intensity exists, the peak features are completely washed out. This indicates that, instead of a simple attenuation by the Co atom adsorption, the QWSs have been destroyed locally. Our results shown in Fig. 2(b) imply that the interaction between the adsorbed Co atom and the Pb surface is so strong that the Co atom cannot be regarded as a perturbation on the Pb film. Instead, the adsorbed Co atom must be considered to alter the boundary conditions for the electrons within the Pb film. In Fig. 3(c), we speculate one possible interpretation. In order to screen out the magnetic-dipole moment of the Co atom, the electrons surrounding the magnetic impurity will form electron cloud possessing the opposite spins. This collective electron-spin fluctuation around the single magnetic impurities may act as scattering centers and amplify the effect from a single Co atom to modify the boundary conditions of the Pb top surface. Thus, the QWSs can no longer form near the site of the Co atom. We estimated that a scattering center with an energy barrier of ~4 eV and a barrier width of ~1 nm is sufficient to backscatter the QWS electrons. At this stage, we cannot pin down the mechanism for the elimination of the QWSs and further work is required. Since the Kondo resonance in the low-temperature region $T < T_k$ is a pure potential scatterer in the Fermi-liquid theory,[4,24] this leads us to consider the surface Kondo effect induced by single Co atoms.

To investigate the Kondo effect and its dependence on DOS at the Fermi level, we have measured the local electronic spectroscopy near the Fermi level both on the Co atom and off the Co atom (on the bare Pb surface) for two terraces with different Pb thicknesses. As shown in Figs. 4(a) and 4(b), the Fermi level for the 15 ML terrace lies on the shoulder of a QWS peak centered at −0.11 eV, resulting in an enhanced DOS at the Fermi level. In contrast, the Fermi level for the 18 ML terrace lies at the valley between two QWSs at −0.32 and +0.38 eV, providing a low DOS at the Fermi level. The ratio of the DOS at Fermi level for the 15 and 18 ML terraces is around 3–4. The $dI/dV$ curves on the 15 and 18 ML bare Pb terraces show very different shapes, as seen especially clear in Fig. 4(c) within a smaller energy range. The dip at the Fermi level in the $dI/dV$ spectra of the bare Pb surface is not due to the Co adsorption since it was observed on clean Pb surface even before Co deposition. The nature of this dip is beyond the present paper and will be discussed elsewhere.[25]

Here, we focus on the comparison of the $dI/dV$ spectra on the Co atom with those on the bare Pb surface. In addition to the $dI/dV$ spectra taken on the bare Pb surfaces, Fig. 4(c) shows the $dI/dV$ curves taken on single Co atoms adsorbed on terraces of 15 and 18 ML Pb thick. As shown by the dotted line, the $dI/dV$ curve taken on the Co atom adsorbed on the 15 ML Pb terrace (site S1) shows a much reduced intensity as compared to the spectrum on the corresponding bare Pb surface, in particular for energy below the Fermi level. This indicates that by adsorption of a Co atom, some of the bare film electronic states in the QWS peaks are now removed and redistributed to the QWS valleys. These distinctive spectra are consistent with our observation of the suppression of QWSs by the single Co atom adsorption. Similarly, on the 18 ML Pb terrace, adsorption of Co destroys the QWSs, but, this time, the intensity of the $dI/dV$ spectrum is increased, indicating that some of the forbidden electronic states caused by the quantum interference in the bare film are now allowed. In another words, the decreased number of electronic states near Fermi level (redistributed to QWS peaks nearby) by quantum interference in the bare 18 ML film is now returned upon Co adsorption. Surprisingly, the spectra on the Co atom adsorbed on both 15 and 18 ML high terraces, shown by the dotted line and triangle line (data points in triangles), respectively, are practically the same, in strong contrast to the large DOS difference caused by QWSs in the same energy region for the bare films. This again supports that the QWSs are completely suppressed. The asymmetric line shape with a dip below the Fermi level and a hump above the Fermi level is a signature of Kondo effect, as reported for a number of other magnetic atoms adsorbed on metallic surfaces.[6,7,9] Such a Kondo line-shape feature was not clearly shown in Fig. 2(b) due to the lower energy resolution and lower differential conductance used there. Using the Fano line-shape formula,[3,4,9]

$$\frac{dI}{dV} \propto \frac{(q+\tilde{\varepsilon})^2}{1+\tilde{\varepsilon}^2},$$

where $\tilde{\varepsilon}=(eV-\varepsilon_K)/\Gamma$, $e$ is the electron charge, $V$ is the bias voltage, $q$ characterizes the line shape, $\varepsilon_K$ is the energy position of the resonance with respect to the Fermi level, and $\Gamma$ determines the half width of the Kondo resonance and the Kondo temperature ($\Gamma=2k_BT_K$); we have fitted the $dI/dV$ curves on the single Co atoms on the 15 and 18 ML Pb terraces. We find that $T_K \sim 100 \pm 10$ K, $q \sim 0.5 \pm 0.05$, and $\varepsilon_K \sim -5$ meV can fit the data quite well for both cases [thick gray line in Fig. 4(c)]. The Kondo temperature obtained here may have been overestimated by ~15% due to the smoothing procedure for both cases since the same smoothing procedure is used. Within the experimental uncertainty, the Kondo resonance of Co atom on both 15 and 18 ML Pb terraces clearly does not exhibit any noticeable thickness dependence.

Our observation on the Kondo effect of Co atom is different from the recent report for MnPc on the same metal host, Pb films,[22] for which a clear dependence of the Kondo resonance on the Pb film thickness was observed. The line shapes of the Kondo resonance for Co and MnPc are also very different and are described by Fano line shape for Co but by Doniach–Sunjic line shape for MnPc. We speculated that the different behaviors are due to the strong interaction between the single Co atom with Pb surface, in contrast to the weak interaction between MnPc and the Pb surfaces. In the case of Co atom, it has two electrons in the $s$ orbital and seven electrons in the $d$ orbital. All these electrons can interact with the Pb surface. However, for MnPc molecule the $s$ orbital in $Mn^{2+}$ is empty and the interaction between $Mn^{2+}$ and the Pb surface is mostly from the $dz^2$ orbital.[22] After forming bonds with the Pc ligands, it is expected that the interaction from the $d$-orbital electrons with the Pb surface is significantly weaker. This speculation is supported by the contrast between our observation of QWS suppression by Co adsorption and their observation of the intactness of QWSs by MnPc molecule adsorption.[22]

## IV. CONCLUSIONS

In summary, we have investigated the electronic structure changes induced by adsorption of single Co atoms on the Pb island and/or film grown on Si(111)-7×7. The quantum well states observed on the clean Pb island were found to be destroyed by the single Co atom adsorption. The spectra near the Fermi level taken on the single Co atoms have shown a different line shape from those on the bare Pb surface, indicating the existence of a Kondo resonance. The large difference in the DOS at Fermi level on the clean terraces with different Pb thicknesses induced by the QWSs does not lead to a significant difference in the Kondo effect of single Co atoms, supporting the notion of the QWS suppression under Co atom. Our results indicate that the interaction strength between an adsorbate and the Pb surface is critical for affecting the robustness of the QWSs.

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