Manipulating the Kondo Resonance through Quantum Size Effects

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(Received 13 September 2007; published 20 December 2007)

Manipulating the Kondo effect by quantum confinement has been achieved by placing magnetic molecules on silicon-supported nanostructures. The Kondo resonance of individual manganese phthalocyanine (MnPc) molecules adsorbed on the top of Pb islands was studied by scanning tunneling spectroscopy. Oscillating Kondo temperatures as a function of film thickness were observed and attributed to the formation of the thickness-dependent quantum-well states in the host Pb islands. The present approach provides a technologically feasible way for single spin manipulation by precise thickness control of thin films.

DOI: 10.1103/PhysRevLett.99.256601 PACS numbers: 72.15.Qm, 68.37.Ef, 68.55.−a, 82.37.Gk

The Kondo effect, arising from the exchange interaction between the localized spins of magnetic impurities and the conducting electrons in the host metal, is one of the most widely studied problems in solid state physics in the past four decades [1,2]. Recent advances in nanotechnology have enabled the observation and understanding of the effect down to a single atomic or molecular level [3–16]. For future applications such as in spintronics and quantum information processing, one needs to control the spin-electron interaction in a nondestructive and reversible manner. In this Letter, we demonstrate such a capability by exploiting the quantum size effects (QSE) in ultrathin Pb films grown on a Si(111) substrate. The behavior of the conducting electrons in Pb thin films, which exhibits well-defined QSE due to the strong confinement, can be precisely regulated by varying the film thickness layer by layer. We study the Kondo resonance of individual manganese phthalocyanine (MnPc) molecules adsorbed on such thin films using a cryogenic scanning tunneling microscope (STM).

Our experiments were conducted with a Unisoku UHV ^{3}He STM system that reaches a base temperature of 0.4 K by means of a single-shot ^{3}He cryostat. Magnetic field up to 11 T can be applied perpendicular to the sample surface. The Si(111) substrate (n-type with a resistivity of 1–5 mΩ cm) was cleaned using the standard procedure at a base pressure of 1.2×10^{-10} Torr [17]. The Si(111)-Pb$\sqrt{3} \times \sqrt{3}$R30° surface was prepared by depositing 3–4 monolayers (ML) of Pb followed by annealing to 300 °C. On this surface, wedge shaped Pb islands with thickness from several ML (1 ML $\sim$ 0.3 nm) to 40 ML were grown [18]. The MnPc molecules (Aldrich Inc.) were then thermally sublimed onto the Pb islands at $\sim$77 K. A polycrystalline PtIr STM tip was used in the experiments.

The MnPc molecules self-assemble into ordered monolayers [Fig. 1(a)] with a square lattice pattern forming a 4×4 superstructure on the Pb(111) islands. Each molecule is imaged as a uniform four-lobe structure with a protrusion on the center. With the STM tip, individual MnPc molecules [indicated by the arrows in Fig. 1(a)] were obtained by dragging them one by one out of the ordered molecular monolayer and moved to a preferential adsorption site on the Pb island. Because of its flattop geometry, the thickness of the Pb island varies by one atomic layer on every successive silicon terrace [Fig. 1(b)].

Scanning tunneling spectroscopic (STS) measurement was subsequently performed on the same molecule but with a different number of Pb atomic layers underneath. In Fig. 1(c), we show a series of dI/dV spectra taken on the center of the MnPc molecule as a function of the film thickness [19]. For each spectrum, a peak near the Fermi energy E_F (at zero bias) is revealed. Similar to previous studies [3–16], we interpret those peaks in Fig. 1(c) as the Kondo resonance due to spin-flip scattering. Distinctly, there is a dramatic change in the width of the resonance for the same molecule even when the film thickness varies by only one atomic layer.

In fitting the data, we found the profile of the well-known Fano function [20] is not sharp enough to faithfully characterize the curves in Fig. 1(c) at the top of the resonance. A better expression for the spectral density, called Doniach-Sunjic line shape, has been available [21]:

$$D(\epsilon) \propto \mathrm{Re}\left(\sqrt{\frac{i\Gamma_K}{\epsilon + i\Gamma_K}}\right). \qquad (1)$$

The resonance width Γ_K is proportional to the characteristic Kondo temperature T_K, $\Gamma_K = 1.545 k_B T_K$. Equation (1) can accurately describe the Kondo resonance exhibiting in the numerical solution of the Anderson model [21,22]. The Doniach-Sunjic line shape itself does not take into account the quantum interference effect [23], which

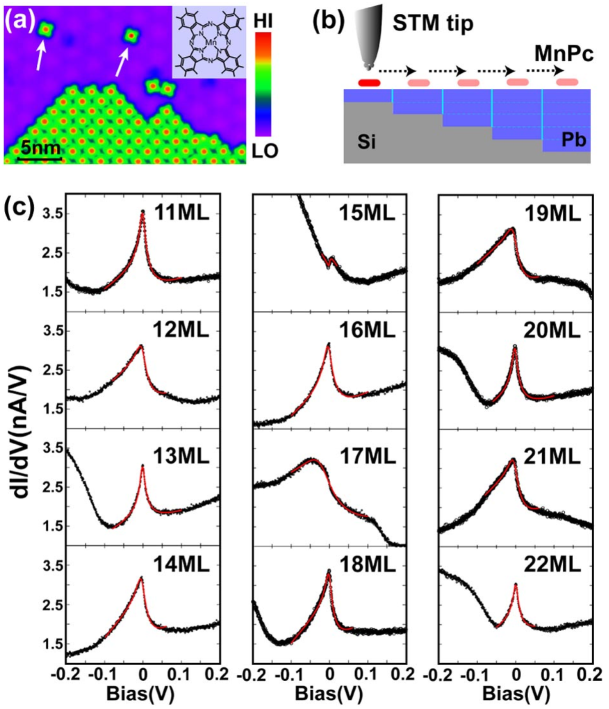

FIG. 1 (color online). Kondo resonance of a MnPc molecule on a Pb island. (a) The self-assembled monolayer of MnPc molecules on Pb(111). The inset shows the schematic molecular structure of MnPc. The hexagonal moiré pattern originating from the Pb/Si interface is clearly resolved on the Pb(111) surface. Imaging conditions: $V = 0.1$ V, $I = 0.1$ nA. (b) Schematic showing how the MnPc molecule could be moved to various thicknesses of the Pb island by manipulation with the STM tip. A bias voltage ~ 0.1 V and a current of 2–3 nA were used for the manipulation. (c) Kondo resonance of the MnPc molecule. The temperature $T = 0.4$ K. The solid curves depict the fitting of the Doniach-Sunjic line shape to the data. The tunneling gap was set at $V_{\text{bias}} = 100$ mV, $I = 0.2$ nA. The bias modulation was 2 mV (rms) at 2 kHz.

leads to the asymmetric profile as in the Fano formalism. Nevertheless, the asymptotic behavior of the peaks in Fig. 1(c) indicates that the sloped background due to the quantum-well states discussed later has significant contribution to the asymmetry in the spectra. The applicability of Eq. (1) with a linear slope as the background is demonstrated by the fitting in Fig. 1(c).

Shown in the upper panel of Fig. 2(a) is the fitted Kondo temperature at different thicknesses, which oscillates with a well-defined period of 2 ML. The lowest (23 K) and highest (419 K) T_K occur at 15 ML and 17 ML, respectively. The error bars in Fig. 2(a) take into account the deviation of T_K induced by the heterogeneity in the electronic structure associated with the moiré pattern (the purplelike periodic hexagons on bare Pb) seen in Fig. 1(a).

To understand the thickness-dependent Kondo temperature, we did STS measurement on the bare Pb(111) island. The STS in Fig. 2(b) clearly reveals the formation of quantum-well states (QWSs) [24] due to the strong quantum confinement of electron motion along the film normal direction. A series of well-defined peaks reflects the quantization of the $6p_z$ band of Pb. These QWSs shift progressively in energy as the film thickness changes by each atomic layer. For every two-monolayer increase in the thickness, an unoccupied QWS moves below the Fermi level and becomes occupied [25]. The structure of the energy spectra exhibits essentially a 2 ML period oscillation. As shown in earlier studies [18,26–28], many physical properties of the film display similar oscillatory behavior. Here we show that it also exists for the Kondo effect.

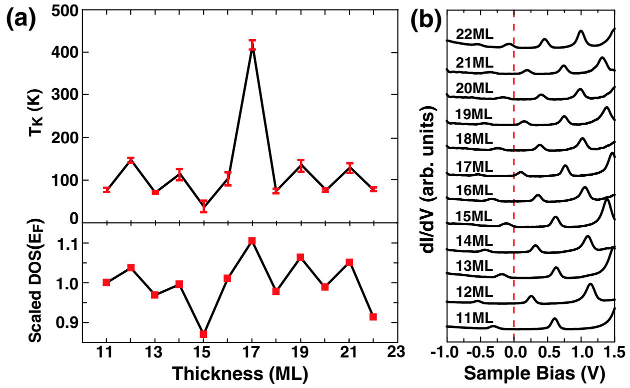

FIG. 2 (color online). Kondo temperature and QWSs. (a) Kondo temperature T_K (upper panel) and density of states (DOS) at Fermi energy (lower panel) as functions of film thickness. T_K has been evaluated on the molecule located at the different positions relative to the moiré pattern. The error bars indicate the variation of T_K due to the moiré pattern. The DOS was measured on a bare Pb island with -0.4 mV bias and 0.1 nA current and averaged over a sufficiently large area on each thickness. The modulation frequency and amplitude were 2 kHz and 3 mV. (b) Differential conduction (dI/dV) spectra of Pb island for different thicknesses measured at a temperature of 4 K. The peaks correspond to the positions of quantum-well states, and the Fermi level (E_F) is indicated by dashed (red) line. The dI/dV signal was recorded at a tunneling gap of $V = 1$ V and a current $I = 0.1$ nA. A modulation at 2 kHz and 20 mV (rms) amplitude was added to the sample bias.

Within the Kondo model, the Kondo temperature T_K can be expressed in the form [1]

$$T_K \sim e^{-1/\rho J}, \tag{2}$$

where ρ and J are the density of states at the Fermi energy and the exchange coupling between the spin of the adsorbed molecule and that of the host, respectively. ρ is modulated by the formation of QWS, which is clearly shown by the STS measurement [lower panel of Fig. 2(a)]. The variation of T_K is related to that of the density of states ρ by

$$\frac{\Delta T_K}{T_K} \sim \frac{1}{\rho J}\frac{\Delta \rho}{\rho}, \tag{3}$$

where ρJ can be estimated via the Schrieffer-Wolff transformation which gives [1]

$$\rho J \sim \Gamma\left(\frac{1}{|\epsilon_d|} + \frac{1}{|U + \epsilon_d|}\right). \tag{4}$$

In Eq. (4), Γ ($\sim$0.1 eV typically), ϵ_d (~ -1 eV), and U ($\sim 2|\epsilon_d|$) are the width, the position, and the on-site Coulomb energy of the impurity's energy level, respectively, which leads to $\Delta T_K/T_K \sim 100\%$ with $\Delta\rho/\rho \sim 10\%$. Equations (2)–(4) indicate that the QWS-modulated density of states at Fermi energy can account for the observed oscillation of Kondo temperature. Although J is considered to be less affected by the QWS in general, it might help explain the high Kondo temperature at 17 ML where a quantum-well state happens to cross the Fermi energy [Fig. 2(b)].

The electronic structure of an adsorbed MnPc molecule was studied by the first-principles simulation using the VASP code [29], which shows that the molecule preferentially adsorbs on the Pb surface when the Mn^{2+} ion sits on the top site. Strong chemical bonding is formed between the dz^2 orbital of the Mn^{2+} ion and the p_z orbital of the Pb atom beneath. Upon adsorption, the magnetic moment of MnPc is reduced from $3\mu_B$ of an isolated molecule [30] to $0.99\mu_B$. Only the magnetic moment from the d_{xy} orbital is well preserved because of its weaker hybridization with the host energy bands.

The possibility of assigning the observed peaks to molecular orbitals can be excluded by the fact that a MnPc molecule on an oxidized Pb island displays no resonance. This situation is shown in Figs. 3(a)–3(c), where the molecules were adsorbed on partially oxidized Pb islands [18]. When a MnPc molecule was moved from the Pb surface [Fig. 3(a)] onto the PbO by the STM tip [Fig. 3(b)], the Kondo peak essentially disappeared [Fig. 3(c)] since the oxide spacer greatly reduces the exchange interaction between the conducting electrons and the localized spins.

To unequivocally attribute the resonance to the Kondo effect, we measured the Zeeman splitting of the peaks as a function of the magnetic field, which is given by $\Delta = 2g\mu_B B$, where $\mu_B = 58\ \mu\text{eV}/T$ is the Bohr magneton and $g = 2.0023$ for a free electron. The width of resonance for an individual MnPc molecule is too wide to observe the splitting. However, the peak widths for different molecules in a MnPc self-assembled monolayer vary prominently due to the lattice mismatch between the molecular 4×4 superstructure and the Pb(111)-(1×1), and the variation forms a periodic pattern. One MnPc inside the monolayer with very low T_K was selected to measure the Zeeman splitting, which is proportional to the magnetic field [Figs. 3(d) and 3(e)]. Fitting the data to a line gives $g = 1.957$, which deviates noticeably from that of a free electron due to the local chemical environment of the Mn ion, similar to the discussion in the context of electron paramagnetic resonance.

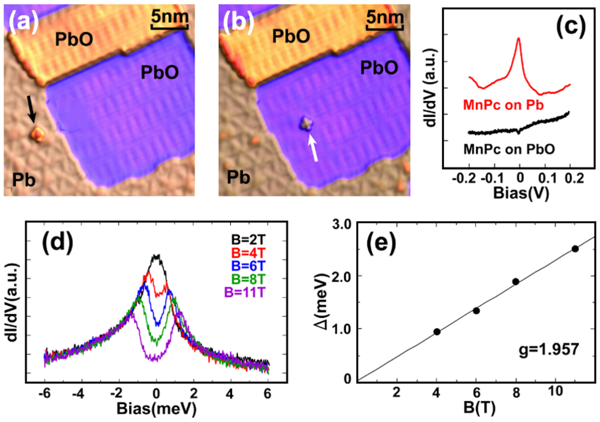

FIG. 3 (color online). (a)–(c) Quenching of Kondo resonance by oxide spacer. PbO patches (the orange and purple regions) of 2 ML thick were prepared on the Pb island surface (the tan regions). A MnPc molecule on Pb [indicated by the arrow in (a)] was moved to an oxidized area [indicated by the arrow in (b)] by the STM tip. The molecule has the same appearance on both oxide and metal. (c) STS of the molecule on bare Pb and oxide. The resonance disappears on oxide because of the decoupling by the PbO layers. The small dip at zero bias exists on both MnPc molecule and bare oxide and is not clearly understood yet. The images were acquired at a sample bias of 0.1 V and a tunneling current of 0.1 nA. For the STS measurement the tunneling gap was set at 0.1 V bias and 0.2 nA current. (d),(e) The Zeeman splitting of Kondo resonance. The MnPc molecule was inside a molecular monolayer on 12 ML of Pb.

The spatial mapping of Kondo resonance provides more insight into the Kondo system [10]. Intuitively, the intensity of the Kondo effect spatially depends on the accessibility of the local spin-flipping channels and can reflect the symmetry of the relevant electronic states. The topography of a MnPc molecule and the simultaneously acquired dI/dV image with a bias on the resonance are shown in Figs. 4(a) and 4(b), respectively. The resonance is found to be localized on the central part of the molecule. Its spatial distribution has fourfold symmetry, which is consistent

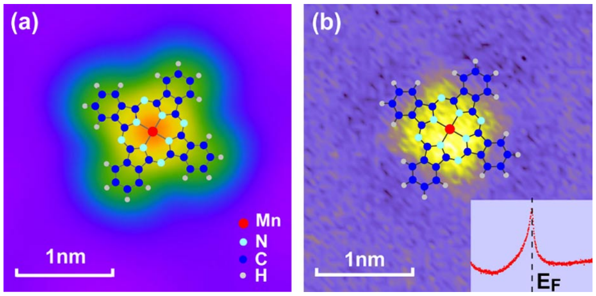

FIG. 4 (color online). (a) Topography and (b) simultaneously acquired dI/dV mapping of a MnPc molecule adsorbed on the Pb island of 11 ML thickness. The molecular structure is superimposed on the images. The inset shows the Kondo peak at the center of the molecule. Imaging conditions: −0.1 V bias and 0.1 nA (topography), −3 mV bias (dI/dV mapping).

with that of the π orbital of a Pc ring that includes four pyrrole nitrogen atoms and four azamethine nitrogen atoms. The Kondo mapping indicates that the Pc ring, besides the central Mn ion, participates in the formation of the Kondo resonance.

In summary, we have devised a Kondo system where the electronic structure of the host metal could be tuned and determined in a direct and well-defined manner. Previously, various stimulating schemes were explored to control the Kondo effect at a single atomic or molecular level by ligand attachment [10], dehydrogenation [11], conformation change [12], or molecular or atomic assembling [6,13]. Most of these studies focus on manipulating the localized spin centers instead of the host conducting electrons. It is difficult to generalize the approaches to other systems since they rely on the specific properties of the spin centers. What we have shown represents a more technologically feasible way to modulate the Kondo resonance by the quantum confinement of a nanostructure whose physical size can now be precisely and conveniently tuned with current nanotechnology. The quantum size effect in precisely tailored nanostructures provides a general platform to manipulate the spin degree of freedom at a single molecular level, and thus opens a new avenue for the study along this direction. The extension to more complex magnetic systems and custom-engineered nanostructures is envisioned, which may lead to a deeper understanding of organic magnetism and find applications in the emerging molecule-based spintronics.

We thank B. F. Zhu, W. Ho, H. Z. Lu, and T. Xiang for discussions. The work is supported by the Ministry of Science and Technology and National Natural Science Foundation of China.

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