Dispersion and Localization of Electronic States at a Ferrocene/Cu(111) Interface

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(Received 7 June 2011; published 14 November 2011)

Low-temperature scanning tunneling microscopy and spectroscopy combined with first-principles simulations reveal a nondissociative physisorption of ferrocene molecules on a Cu(111) surface, giving rise to ordered molecular layers. At the interface, a 2D-like electronic band is found, which shows an identical dispersion as the Cu(111) Shockley surface-state band. Subsequent deposition of Cu atoms forms charged organometallic compounds that localize interface-state electrons.

DOI: 10.1103/PhysRevLett.107.216801 PACS numbers: 73.20.At, 68.37.Ef, 71.15.Pd, 73.20.Hb

Further progress in realizing functional metal-molecule junctions for future electronic devices relies on our understanding of the electronic states at the interface [1]. In particular, delocalized interface states near the metal Fermi level are considered a key ingredient for tailoring charge injection [2,3]. Interfacial electron delocalization depends on a large number of chemical, structural, and morphological parameters, all influencing the spatial extension of the electron wave function [3]. It is therefore important to determine to what extent these parameters impact the electron behavior at the interface.

Recent studies [4–8] have evidenced the formation of a 2D-like interface state upon the adsorption of planar purely organic molecules on metal surfaces. Although the link between this state and the Shockley surface state of metal has been underlined in photoemission studies [5–7], its robustness to atomic-scale modifications of the molecular layers remains unaddressed. In particular, it is still unclear how such an interface state responds to a subsequent exposure to single metal atoms, as for example, in the initial stage of growth of a top electrode.

In this Letter, we show that a double-decker organometallic compound, namely, the ferrocene $[Fe(C_5H_5)_2]$ molecule, can be deposited on a Cu(111) surface without any decomposition. This provides a versatile system to investigate the adsorption and the interface states at a metal-organometallic interface. Compact layers of ferrocene are shown to produce a 2D-like interface state strongly resembling the Shockley surface state of copper. By a subsequent deposition of single metal atoms on the molecular layer, we analyze the sensitivity of the interface state to local modifications of the interface potential. Experiments are combined with first-principles dynamical simulations to provide an insight into adsorption and charge redistribution processes. Our findings demonstrate the feasibility of exploiting the chemical reactivity of molecules to modify the electron behavior at a metal-molecule interface.

The measurements were performed in a low-temperature STM operating below 10^{-10} mbar and at 4.6 K. The Cu(111) single crystal was cleaned by repeated cycles of Ar^+ sputtering and annealing up to 800 K. About 0.7 monolayers (ML) of ferrocene were dosed at room temperature onto a precooled Cu(111) substrate (< 200 K) at a rate of 0.04 ML s^{-1}. The ferrocene molecules $[Fe(C_5H_5)_2]$ adsorb on one of the two C_5H_5 (cyclopentadienyl, Cp in the following) rings and form large compact islands, as can be observed in Fig. 1(a). Single metal atoms were evaporated

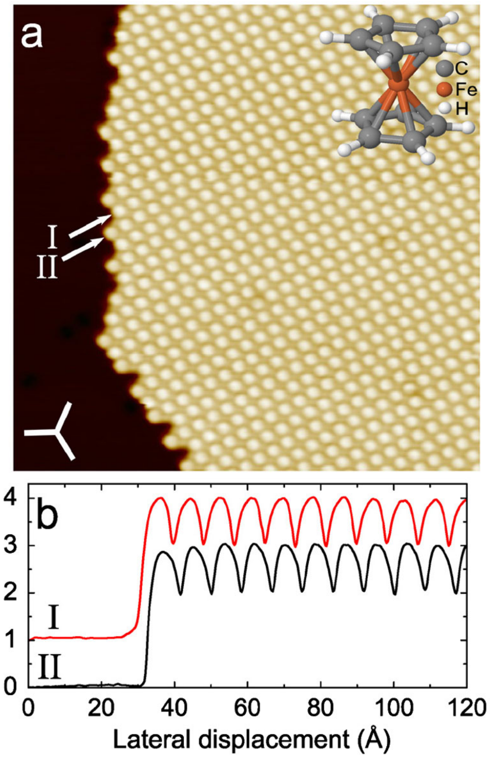

FIG. 1 (color online). (a) STM image (size: 250×250 Å^2, -0.5 V, 0.5 nA) with thick white lines indicating the close-packed crystallographic directions of the Cu(111) surface. Inset: Model structure of the ferrocene molecule. (b) Line profiles along row I and II. The profile along row I is displaced upward by 1 Å for clarity. The apparent height of 3 Å is in good agreement with Ref. [15].

onto the sample through an opening in the radiation shields of the STM. The differential conductance (dI/dV) as a function of sample bias (V) was acquired via lock-in detection with a bias modulation of 5 mV rms at 5 kHz. A variety of etched W tips were employed. All tips were treated *in vacuo* by sputter/anneal cycles and then by soft indentations into the clean copper surface. The well-known steplike onset of the Cu(111) Shockley surface state appeared then as a sharp and reproducible feature [see Fig. 3(a)].

Despite a few studies, mostly performed by photoemission spectroscopy [9–12], on the adsorption of ferrocene on metal surfaces, STM experiments are limited to the imaging of ferrocene derivatives [13,14]. One STM study, interestingly, showed that ferrocene dissociates on a Au(111) surface forming complex layered structures [15]. At variance with those results, our study reveals that the integrity of the ferrocene is preserved upon adsorption on Cu(111), reflecting a weaker interaction with Cu than with Au. As shown in Fig. 1, only one molecular species is observed and this feature is present on all samples examined. The molecules assemble into two alternating rows, both aligned perpendicularly to one close-packed direction of Cu(111) [Fig. 1(a)]. Moreover, the sawtoothlike shape of the line profiles taken along two neighboring rows indicates a tilt of the molecules in opposite directions, as can be observed in Fig. 1(b). While in a constant-current image [Fig. 2(a)] the tilt is barely detected, the dI/dV map [Fig. 2(b)] clearly highlights a similar tilt within rows and an opposite one among adjacent rows.

To complement experiments and to disentangle molecular collective effects from the atomic-scale origin of the adsorption of ferrocene, we performed first-principles dynamical simulations [16] within both a Born-Oppenheimer approach and a free energy molecular dynamics scheme [17,18] at a temperature of 150 K. The surface is modeled by a periodically repeated slab of 420 Cu atoms, amounting to five layers. This results in an exposed area of 17×26 Å^2 on which ferrocene molecules can evolve dynamically. In the first simulation, a single molecule was allowed to equilibrate on the Cu(111) surface for about 3.0 ps. The molecule is adsorbed in a nondissociative way, with one of the two Cp rings centered on top of a Cu atom of the surface at an average distance of 3.7 Å [Fig. 2(c)]. This configuration is stabilized after 1.2 ps. A subsequent dynamics scheme involving two ferrocene molecules was run for 7.0 ps. The second molecule, added beside the one stabilized during the first dynamics run, aligns along one crystallographic direction of the surface. Moreover, as shown in Fig. 2(c), the molecules tilt their axis roughly 10° with respect to each other, in agreement with experimental observations. The reason for the tilt is the steric repulsion of the H atoms of the Cp rings. Such a repulsion is also responsible for in-plane molecular rotations on Cu(111) (see Fig. S1 in the Supplemental Material [18]). Based on the computational results and STM images, including experimental-resolved atomic

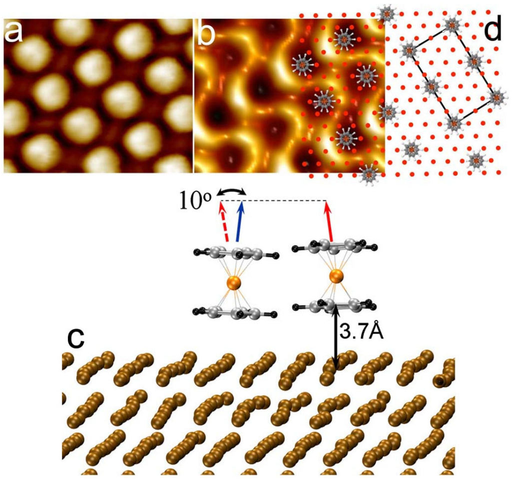

FIG. 2 (color online). (a) Close-up view STM image (34×28 Å^2, -0.5 V, 5.0 nA) of the molecular layer. (b) dI/dV map of the same area (-1.4 V, 1.0 nA). (c) Stable configuration of two ferrocene molecules on the Cu(111) surface obtained via dynamical simulations. (d) Adsorption model for the ferrocene monolayer and its unit cell, which takes into account the tilt of the molecules.

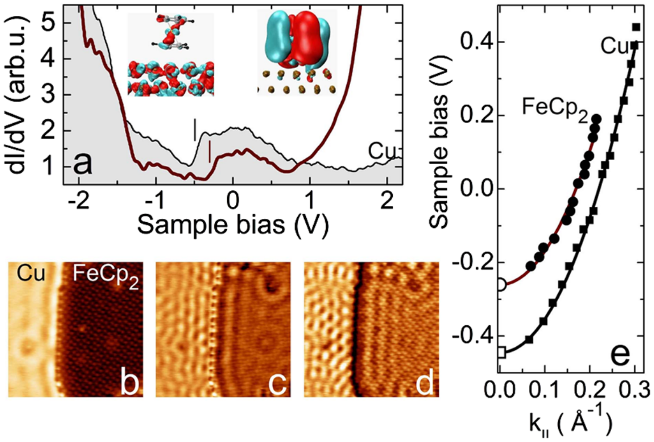

FIG. 3 (color online). (a) dI/dV spectra for the clean Cu(111) surface (thin line) and the ferrocene monolayer (thick line). Vertical ticks indicate the onsets of the Shockley surface state and of the interface state. Insets: calculated HOMO and LUMO states for a ferrocene molecule equilibrated on top of the Cu(111) surface. Positive (red [dark gray]) and negative (cyan [light gray]) isosurfaces are at 5×10^{-3} $(e/\text{Å}^3)^{1/2}$. (b)–(d) dI/dV maps of the same area near a monolayer border, showing the standing-wave patterns at sample biases of -0.35 V, -0.15 V and -0.10 V, respectively. (e) Dispersion of the Cu(111) Shockley surface state (full squares) and of the interface state (full circles). The open circle and square at $k = 0$ correspond to the onsets measured in the dI/dV spectra of ferrocene monolayer and Cu(111) surface, respectively. The full lines are parabolic fits.

lattice of the Cu(111) surface close to the molecular layers (not shown here), an adsorption model is proposed in Fig. 2(d).

To verify the impact of these structural details on the electronic states, we performed dI/dV spectroscopy at various positions above the monolayer, but intriguingly, all spectra are identical between -2.5 V and 2.5 V. Moreover, as shown in Fig. 3(a), the spectrum measured above the monolayer has common features with the spectrum acquired on the clean Cu(111) surface. Over the monolayer, marked upturns in the spectrum are measured only for large biases. This suggests a significant preservation of the HOMO-LUMO gap [9,19] (HOMO: Highest Occupied Molecular Orbital, LUMO: Lowest Unoccupied Molecular Orbital). Since for positive biases, the Cu(111) spectrum is featureless, we associate the increase of the dI/dV for biases above 0.75 V to the tunneling into the LUMO lower edge. For negative biases an upturn of the line at -1.25 V is measured for both the Cu(111) surface and the ferrocene monolayer. Therefore, it is difficult to disentangle the contribution of the molecular HOMO from that of Cu(111) bulk states. To clarify this, we inspected the calculated electronic structure of an adsorbed ferrocene molecule. As shown by the two insets in Fig. 3(a), the LUMO wave functions are strongly localized on the molecule. Conversely, the HOMO is composed of a mixture of molecular and substrate contributions, thus explaining the dI/dV features measured below -1.25 V [Fig. 3(a)]. Nonetheless, right below the Fermi level a clear steplike onset falling at -0.26 V is observed for the monolayer. This feature strongly resembles the well-known onset of the Shockley surface state of the Cu(111) surface ($-$ 0.44 V) [see the Cu spectrum in Fig. 3(a)].

To better understand the origin of the steplike feature observed in the dI/dV spectrum of ferrocene [Fig. 3(a)], we checked the dispersion of the electronic states by recording dI/dV maps at different sample biases [Figs. 3(b)–3(d)]. The observed standing-wave patterns, which reflect the quantum behavior of two-dimensional electron gases at surfaces [20], evolve with the applied bias on both ferrocene and Cu(111). Note that between the two onsets indicated in Fig. 3(a) standing waves are observed only for the Cu(111) surface [Fig. 3(b)]. A careful analysis of several dI/dV maps shows that, upon adsorption of ferrocene, the Cu(111) Shockley surface-state band ($\lambda_F = 29$ Å) transforms in a 2D-like interface-state band with a larger wavelength of $\lambda_F = 37$ Å. These values are extracted from the dispersion curves [Fig. 3(e)] obtained by fast Fourier transform of bias-dependent dI/dV maps acquired over large sample areas [21]. The energy shift between the two bands amounts to $\delta E = 0.18$ V in Fig. 3(e), and can be understood within models accounting for changes of the confinement potentials at a crystal surface [22–26]. Based on our energy shift and exploiting the predicted linear relation with the adsorption energy [27], we estimate the physisorption of a ferrocene molecule on Cu(111) to be 140 meV [18]. This is in good agreement with the value of 120 meV computed from our simulations [18].

A significant particularity of the interface state observed here should be emphasized. By fitting the experimental data in Fig. 3(e) with the standard dispersion $E = E_0 + (\hbar k_{\|})^2/2m^*$, we find a full preservation of the electron effective mass of $m^* = (0.40 \pm 0.01)m$, m being the free electron mass. Consequently, the $\delta E = 0.18$ V upward shift of the Shockley state band is independent of the $k_{\|}$ values over the energy range considered here. Therefore, the confinement potentials remain unmodified upon adsorption of ferrocene. The only effect produced by the molecular layer is to localize the image potential closer to the crystal surface due to the polarizability of the molecules. This reduces the 2D potential well and consequently shifts the band to higher energies, as also concluded in [5]. The dispersion of the interface state remains dominated by the crystal potential as predicted by the phase-accumulation model [22]. These conclusions are also supported by our first-principles simulations showing a delocalized quasi-2D electronic state at the Cu(111) surface with negligible overlap with the ferrocene electronic density ($\rho(r) < 3 \times 10^{-4}$ $e/\text{Å}^3$) [18].

To further assess the response of this interface state to modifications of the interface potentials we deposited single metal atoms on the ferrocene monolayer. Copper atoms are captured by the upper Cp rings resulting in new Cu-FeCp$_2$ organometallic compounds [Figs. 4(a) and 4(b)]. The atoms are easily recognizable in the STM images as round dots

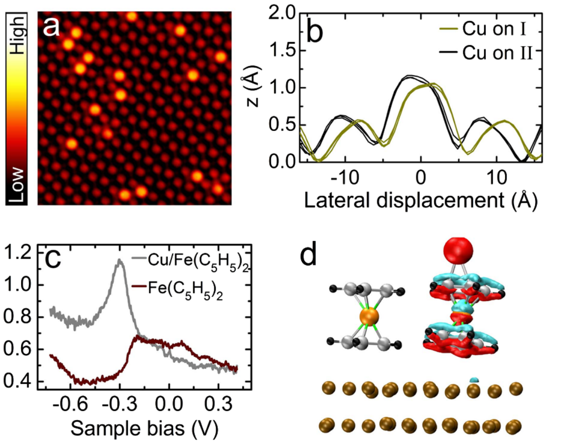

FIG. 4 (color online). (a) STM image of Cu atoms adsorbed on a ferrocene monolayer (size: 120×120 Å^2, -0.05 V, 5 pA). (b) Line profiles across adsorbed copper atoms on row I and II. (c) dI/dV spectra of ferrocene monolayer and of a copper atom adsorbed on ferrocene, in a bias range near the onset of the interface state ($-$ 0.26 V). (d) Electron density difference computed as described in the text. Positive (red [dark gray]) and negative (cyan [light gray]) isosurfaces at 5×10^{-2} ($e/\text{Å}^3$) reveal regions with a lack and excess of electronic charge, respectively.

[Fig. 4(a)] sitting in the center of the Cp rings. An equal number of atoms are found on the two rows. The atoms are imaged as protrusions about 7 Å wide and less than 1 Å high [Fig. 4(b)]. The line profiles across the atoms also confirm their central position on the Cp rings. The dI/dV measurements performed above these atoms reveal that the onset of the interface-state band is replaced by a resonance falling at a slightly lower bias [Fig. 4(c)]. A similar feature is detected in the case of single Au atoms on the ferrocene monolayer (not shown). The energetic position of the resonance strongly suggests a localization of the interface-state electrons induced by the potential of the molecular compound. This scenario resembles the case of adatoms on clean metal surfaces [28–30] or salt overlayers [31,32]. As established in Ref. [28], an attractive perturbation of the confinement potential leads to the appearance of a localized state—a bound state split off from the bottom-edge band. This indicates that the Cu atoms captured by the ferrocene molecules induce charge redistributions so as the electrons within the interface-state band experience an attractive potential at the site of the Cu-FeCp$_2$ compound.

To analyze this charge redistribution, we first verified by dynamical simulations the stability of a Cu atom on top of a ferrocene molecule. Starting with a Cu atom at an initial distance of 3.0 Å from one of the top Cp rings of the two equilibrated molecules, the system stabilizes in about 1.2 ps. The Cu atom sticks to the ring at an average distance of 2.4 Å. Charge redistribution analyses reveal that about 0.3e are transferred from the Cu atom to the ferrocene/substrate system. This effect is depicted in Fig. 4(d), in terms of an electron density difference computed as $\Delta\rho(r) = \rho(r) - [\rho_0(r) + \rho_{\mathrm{Cu}}(r)]$, where $\rho(r)$ and $\rho_0(r)$ are the total electron density of the system with and without the Cu atom, respectively, whereas $\rho_{\mathrm{Cu}}(r)$ is the electron density of an isolated Cu atom in the same position. In this way the electron-depleted regions are clearly highlighted (red zones). Note that the electron density on the adatom-free molecule is not affected by the presence of a Cu atom on the neighboring molecule. The Cu-FeCp$_2$ compound acquires a positive charge and acts as a charged defect interacting with interface-state electrons near the Γ point. We therefore extend to adsorbed molecules the general concept of a 2D electron-gas localization by an attractive potential [33].

Summarizing, the physisorption of ferrocene on a metal surface such as Cu(111) supports the notion of delocalized interface states formed upon deposition of molecules on surfaces with a Shockley surface state. Single-atom capturing by ferrocene produces a new compound, which localizes the interface state by a local modification of the interface potential. This discloses new ways for tuning interface states by selecting the atom *in* and *on* a metallocene overlayer. Our findings also open up the perspective of studying other structure-related properties in these compounds, such as spin states [34].

M. B. thanks computational resources from PMNA and GENCI under the allocation x2010096092. The authors acknowledge the Agence Nationale de la Recherche (Grant No. ANR-07-BLAN-0139, project SPINMASTER) and the International Center for Frontier Research in Chemistry (FRC) for financial support.

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[1] See, e.g., G. Cuniberti, G. Fagas, and K. Richter, *Introducing Molecular Electronics* (Springer, Berlin, 2005).
[2] J. C. Scott, J. Vac. Sci. Technol. A **21**, 521 (2003).
[3] X. Y. Zhu, Surf. Sci. Rep. **56**, 1 (2004).
[4] R. Temirov *et al.*, Nature (London) **444**, 350 (2006).
[5] C. H. Schwalb *et al.*, Phys. Rev. Lett. **101**, 146801 (2008).
[6] A. Scheybal *et al.*, Phys. Rev. B **79**, 115406 (2009).
[7] K. Kanai, Y. Ouchi, and K. Seki, Thin Solid Films **517**, 3276 (2009).
[8] N. Gonzalez-Lakunza *et al.*, Phys. Rev. Lett. **100**, 156805 (2008).
[9] P. A. Dowben *et al.*, Chem. Phys. Lett. **283**, 44 (1998).
[10] D. Welipitiya *et al.*, Surf. Sci. **367**, 20 (1996).
[11] C. Waldfried *et al.*, J. Phys. Chem. B **101**, 9782 (1997).
[12] C. M. Woodbridge *et al.*, J. Phys. Chem. B **104**, 3085 (2000).
[13] D. Y. Zhong *et al.*, Phys. Rev. B **76**, 205428 (2007).
[14] L. F. N. Ah Qune, K. Tamada, and M. Hara, e-J. Surf. Sci. Nanotechnol. **6**, 119 (2008).
[15] K.-F. Braun, V. Iancu, N. Pertaya, K.-H. Rieder, and S.-W. Hla, Phys. Rev. Lett. **96**, 246102 (2006).
[16] CPMD, Copyright IBM Corp. (1990–2009) and MPI für Festkörperforschung Stuttgart (1997–2001).
[17] A. Alavi, J. Kohanoff, M. Parrinello, and D. Frenkel, Phys. Rev. Lett. **73**, 2599 (1994).
[18] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.107.216801 for details about our dynamical simulations and adsorption energy calculations.
[19] See, e.g., L. Vitali *et al.*, Nano Lett. **8**, 3364 (2008).
[20] M. F. Crommie, C. P. Lutz, and D. M. Eigler, Nature (London) **363**, 524 (1993).
[21] To measure the k values we followed: L. Petersen *et al.*, Phys. Rev. B **57**, R6858 (1998).
[22] N. V. Smith, Phys. Rev. B **32**, 3549 (1985).
[23] J. D. McNeill *et al.*, J. Chem. Phys. **105**, 3883 (1996).
[24] E. V. Chulkov, V. M. Silkin, and P. M. Echenique, Surf. Sci. **437**, 330 (1999).
[25] A. Hotzel *et al.*, Appl. Phys. B **68**, 615 (1999).
[26] J. Repp, G. Meyer, and K.-H. Rieder, Phys. Rev. Lett. **92**, 036803 (2004).
[27] J. Ziroff *et al.*, Surf. Sci. **603**, 354 (2009).
[28] F. E. Olsson *et al.*, Phys. Rev. Lett. **93**, 206803 (2004).

[29] L. Limot, E. Pehlke, J. Kröger, and R. Berndt, Phys. Rev. Lett. **94**, 036805 (2005).

[30] B. W. Heinrich *et al.*, Phys. Rev. B **79**, 113401 (2009).

[31] F. E. Olsson, S. Paavilainen, M. Persson, J. Repp, and G. Meyer, Phys. Rev. Lett. **98**, 176803 (2007).

[32] See also the case of atomic vacancies at salt overlayers: J. Repp *et al.*, Phys. Rev. Lett. **95**, 225503 (2005).

[33] B. Simon, Ann. Phys. (N.Y.) **97**, 279 (1976).

[34] T. Komeda *et al.*, Nature Commun. **2**, 217 (2011).