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Localization of the Cu(111) Surface State by Single Cu Adatoms

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The Cu adatom-induced localization of the two-dimensional Shockley surface state at the Cu(111) surface was identified from experimental and simulated scanning tunneling microscopy spectra. The localization gives rise to a resonance located just below the surface state band edge. The adatom-induced surface state localization is discussed in terms of the existence theorem for bound states in any attractive two-dimensional potential. We also identify adatom-induced resonance states deriving from atomic orbitals in both experimental and simulated spectra.

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Shockley surface states at noble metal surfaces provide an ideal model system for electrons propagating in two dimensions (2D). Direct real space information on these states at the atomic scale is provided by scanning tunneling microscopy (STM), revealing the properties of the surface states from standing wave patterns around defects at the surface. The ability of the STM to assemble nanostructures, such as quantum corrals [1,2], from single adsorbates provides means to tailor the propagation of surface states in confined geometries with potential use in nanotechnology. The scattering of surface states from adsorbates introduces also a long-range adsorbate-adsorbate interaction that affects, for example, growth [3,4]. Thus there is a need to characterize the scattering properties of surface states from elementary defects at surfaces, such as single adatoms. STM and scanning tunneling spectroscopy (STS) have provided detailed information about adatoms interacting with surface states, for example, standing wave patterns around adatoms [5] and Kondo resonances induced by magnetic adatoms [2,6,7].

A most important fundamental physical effect associated with a 2D surface state interacting with an adatom that has not yet been demonstrated is the possibility of an adatom-induced localization of the surface state [8]. The localization is a direct consequence of the 2D character of the surface state. A theorem by Simon [9] states that any attractive 2D potential has a bound state. In an earlier investigation based on model potentials for Cs on Cu(111), we suggested that adatom-induced localization of the surface state may be observed in STS as a peak appearing just below the surface state band edge [10]. Since the 2D surface state is embedded in the 3D bulk states, this peak corresponds to a resonance state decaying into the bulk state continuum rather than to a 2D bound state. The existence of surface state localization by an adatom has not yet been demonstrated for a real system.

In the present work, we present STS experiments combined with detailed theoretical simulations of electronic states for single Cu adatoms on Cu(111) that demonstrate the localization of the Cu(111) Shockley surface state by a Cu adatom. The simulations were carried out in a parameter-free scheme, where the adatom-induced effects on the electronic states were obtained from wave packet and density functional calculations [11]. These calculations show that the observed peaks in the STS data can be assigned to either surface state localization or resonances deriving from atomic orbitals.

In search of experimental evidence for adatom-induced resonances, we carried out low-temperature STM investigations at 7 K. Standard procedures were applied for sample preparation in ultrahigh vacuum as described in Ref. [12]. In the spectroscopic measurement, the differential tunneling conductance dI/dV was recorded at constant STM tip height by conventional lock-in technique. This experimental quantity provides a measure of the local density of states (LDOS) of the sample at the tip apex [13]. dI/dV spectra were measured on top of the adatom and at positions close to the adatom at an estimated tip height of ~ 6 Å.

The STM image in Fig. 1(a) shows a single Cu adatom characterized by an apparent height of 0.7 Å and a full width at half maximum (FWHM) of 5.2 Å at the indicated tunneling parameters; the faint wave pattern around the adatom arises from standing waves of the surface state. As shown in Fig. 1, the topmost dI/dV spectra recorded over the adatom exhibits a clear peak at a sample bias of -0.49 V with a FWHM of ~ 150 mV. With increasing lateral tip displacement, R, this peak rapidly decays in intensity and the Cu(111) surface state band edge evolves. The spectra measured at $R = 25$ Å shows the surface state band edge located at a sample bias of -0.44 V. This value is consistent with the band onset found in previous STS [5] and photoelectron spectroscopy experiments [14,15]. Our STS data thus reveal the existence of an adatom-localized state ~40 meV below the surface state band edge. The single Cu adatom is also associated with a pronounced peak at 3.3 eV relative to E_F [12], as shown by the experimental spectra in the inset of Fig. 2. This sharp resonance is located within the pseudogap of the projected Cu bulk bands, which extends from ~ -0.9 to ~4.25 eV, relative to E_F [16].

To gain detailed insight into the physics underlying these resonances, we have simulated dI/dV spectra by calculating the energy-dependent LDOS at the tip apex, $\mathbf{r}_{\text{tip}}$ [17–19]. The LDOS calculation is based on a wave packet propagation technique, detailed in [20]. A time-dependent wave packet, $\Psi(\mathbf{r}, t)$, is obtained by solving the time-dependent one-electron Schrödinger equation [10,20] with an initial wave packet, Φ_0, that mimics a δ function centered at $\mathbf{r}_{\text{tip}}$ [21]. From $\Psi(\mathbf{r}, t)$ and Φ_0, the LDOS is calculated as the real part of the Laplace transform of the survival amplitude of the system [10].

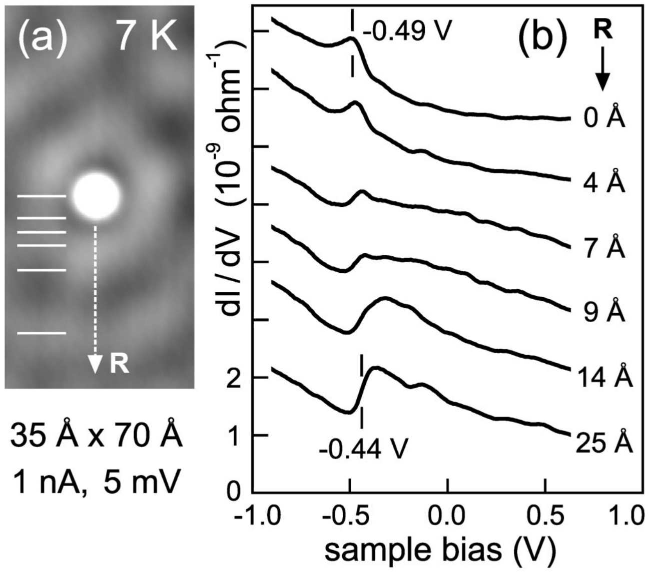

FIG. 1. Experimental STM image and STS spectra. (a): Constant-current STM image of a single Cu/Cu(111) adatom (35 Å × 70 Å, 5 mV, 1 nA, 7 K), the gray scale is enhanced to display the standing wave pattern of the surface state; horizontal white bars mark lateral distances, R, relative to the adatom where the differential tunneling conductance was measured at constant tip height. (b) Corresponding spectra measured with the tip positioned on top of the adatom (topmost curve) and at different lateral distances R as indicated (for clarity, spectra are offset by a constant of $10^{-9}\ \Omega^{-1}$, relative to the lowest curve). Bias-voltage and tunneling current prior to turning off the feedback loop: 1 V, 1 nA; amplitude and frequency of the lock-in modulation: 30 mV, 640 Hz.

The time propagation of the wave packet is performed in cylindrical coordinates (z,ρ,ϕ) using the potential

$$V(z, \rho) = V_S(z) + \Delta V_{\text{ads}}(z, \rho) + U_{\text{field}}. \qquad (1)$$

The z axis is normal to the surface and goes through the adatom center. V_S is a one-dimensional representation of the Cu(111) surface potential, designed to describe the observed band gap, image, and surface state energies at the Γ point [16]. ΔV_{ads} is the adatom-induced potential, which we have obtained through a parameter-free procedure from density functional calculations [11]. Consistent with the choice of V_S, only the $m = 0$ component of ΔV_{ads} was retained (m is the projection of the electron angular momentum on the z axis), whereby only the (z, ρ) coordinates are necessary [22]. The final term accounts for the changes in the potential in a simple capacitor model; U_{field} is equal to 0 for $z < z_0$, $U(z - z_0)/(z_{\text{tip}} - z_0)$ for $z_{\text{tip}} > z > z_0$ and U for $z > z_{\text{tip}}$, where z_0 and z_{tip} are the positions of the surface image plane and tip apex, respectively, and U is the applied voltage. This representation of the applied voltage in dI/dV simulations gives a good description of the shifts of the surface state thresholds observed in dI/dV data for surface and image states [23,24].

The calculation of ΔV_{ads} follows two steps. First, we calculate the electronic structure of the bare Cu(111) surface and of the Cu/Cu(111) system [25] in a supercell geometry using density functional calculations within the local density approximation as implemented in the Vienna *ab initio* simulation package code [27]. The core electrons of the Cu adatom were represented by a nonlocal pseudopotential of Kleinman-Bylander type, V_{PP} [28]. We thus obtain the adatom-induced electron densities, Δn, and

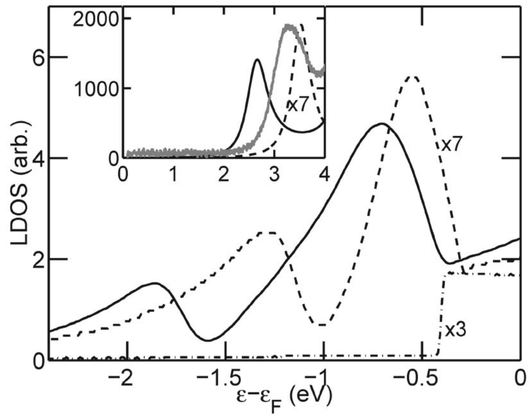

FIG. 2. Calculated LDOS at 6 Å outside the Cu(111) image plane for a Cu adatom on Cu(111) (solid black line) and bare Cu(111) (dash-dotted line). The dashed line is the calculated LDOS with $U = 3.3$ V in Eq. (1). The LDOS for bare Cu(111) and for Cu/Cu(111) with $U = 3.3$ V, have been multiplied by 3 and 7, respectively. Inset: experimental STS (solid gray line) and calculated LDOS for unoccupied states.

adatom-induced one-electron exchange-correlation potentials, ΔV^{xc}, for these systems. Both ΔV^{xc} and Δn are found to be well confined within the 4×4 surface unit cell used in the calculation. Second, by solving Poisson's equation with Δn, we obtain the Hartree potential, ΔV^{H}, induced by a single adatom in the entire space. This scheme ensures that the long-range behavior of ΔV^{H}, that is, the long-range dipole potential, is accurately described. ΔV_{ads} is then given by the sum of ΔV^{H}, ΔV^{xc}, and V_{PP}.

The calculated LDOS for Cu/Cu(111) presented in Fig. 2 exhibits several adatom-induced peaks. Two adatom-induced peaks appear among the occupied states. One at -0.7 eV ($U = 0$), just below the surface state band edge, and another at -1.9 eV ($U = 0$). In the inset we also show the LDOS obtained for the unoccupied states, exhibiting a single peak at $+2.7$ eV ($U = 0$, full line). As will be shown below, the peak at -0.7 eV is assigned to surface state localization by the adatom, whereas the peaks at -1.9 and 2.7 eV are assigned to resonances deriving from the d_{z^2} atomic orbital and sp_z hybrid atomic orbitals, respectively.

To characterize the adatom-induced resonances revealed by the calculated LDOS we have computed their wave functions [8,20], which were obtained from the Laplace transform of the wave packet at the resonance energy. The resonant wave function at $+2.7$ eV, shown in Fig. 3(a), exhibits the characteristic structure of an hybrid state formed from s and p_z orbitals of the adatom with a strong coupling to the metal. As seen by the tail of the wave function extending along the surface, there is a substantial decay of this resonance into the surface state. The resonant wave function at -0.7 eV, shown in Fig. 3(b) is quite different. It is located much closer to the surface image plane and it exhibits a large decay into 3D propagating bulk states. The d_{z^2} character of the resonance at -1.9 eV was characterized in a similar manner using its resonant wave function (not shown).

A complementary characterization of the resonances in the LDOS is provided by their response to a modification of the pseudopotential V_{PP} for the adatom. V_{PP} consists of a local part giving the $l = 0$ component and nonlocal projectors for $l = 1, 2$. We have removed either the $l = 1$ or $l = 2$ nonlocal projectors. Removal of a nonlocal projector of V_{PP} is expected to mainly affect states with a significant component in that symmetry. If the nonlocal projector for the $l = 1$ is removed, only the peak at 2.7 eV was slightly shifted, whereas if the $l = 2$ nonlocal projector is removed, only the peak at -1.9 eV was shifted. In none of these modifications of V_{PP} the peak at -0.7 eV shifted. These observed shifts of the resonances due to changes in V_{PP} then corroborate our previous assignments of the peaks. As another indication of the nature of the surface state threshold peak, we have considered its behavior under an outward displacement of ΔV_{ads}. As ΔV_{ads} is displaced outwards, the peak remains pinned just below the surface state band edge, while becoming more narrow and weaker.

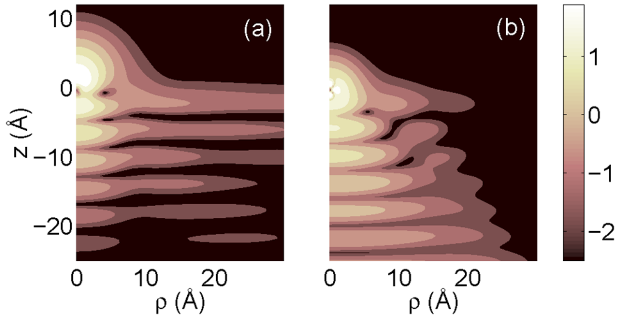

FIG. 3 (color online). Logarithm of the modulus of the resonant wave functions calculated at (a) $E = 2.7$ eV and (b) $E = -0.7$ eV. The adatom center is at the origin of coordinates.

We now turn to a direct comparison between the experimental and simulated dI/dV spectra, in Figs. 1 and 2, respectively. First, the adatom-induced peak appearing just below the surface state band edge in both spectra gives evidence for surface state localization by the adatom. However, the agreement between the experimental and simulated dI/dV peak shapes is only qualitative: the calculated width of the surface state band edge peak, 0.5 eV, is larger than the experimental width, 0.15 eV. This discrepancy is most likely an effect of the approximations in the system modeling, in particular, the choice of the model potential [16] for the bare Cu(111) surface that assumes a free-electron propagation in the direction parallel to the surface and the neglect of a possible local relaxation of the substrate due to the adatom. Second, the agreement for the unoccupied sp_z resonance peak (3.3 V in experiment) is, on the other hand, excellent for a sample bias of $U = 3.3$ V in Eq. (1), as shown in Fig. 2 inset. The d_{z^2} peak in the simulated spectrum is too spatially localized to be resolved in experiment.

The peak energy shift in response to an external electric field in the simulated dI/dV spectrum is important to correctly simulate experimental dI/dV spectra at large bias U. The shift is associated with the average localization of the resonance, whereby it also reflects the origin of the peak. As shown in Fig. 2 for $U = 3.3$ V, the surface state band edge peak does not shift considerably in the applied electric field, whereas the peaks deriving from atomic orbitals have appreciable peak energy shifts. From the bias-induced peak energy shifts, one can get a rough estimate of the average electron position in each resonance, within our simple capacitor model for the electric field ($U = 3.3$ V). The surface state band edge peak, corresponds to an average electron position 0.45 Å below the adatom, which is close to the image plane of the bare surface, as expected for a surface state related structure. The sp_z hybrid, on the other hand, is centered slightly outside the adatom position, as expected for a polarized atomic orbital. The d_{z^2} orbital is basically centered on the adatom.

A prerequisite for a surface state localization is an attractive adatom-induced potential in the region of the adatom-surface state overlap. For a Cu adatom, the adatom core is incompletely screened by the free-electron like electrons of the surface, which results in an attractive adatom-induced potential. This picture is verified by the calculated decrease in work function of 0.35 eV, in the 4×4 surface unit cell.

Adatom-induced peaks below the surface state band have been previously observed by STS in other systems such as Cu and Co on Au(111) [29], Ag on Ag(111) [30], and S on Ag(111) [31]. The widths of the reported resonances are similar to the width of the presently observed experimental peak for Cu on Cu(111). The adatom-induced peaks for Cu and Co on Au(111) have been suggested to derive from a state split-off from the surface state [29]. However, no clear assignment of the origin of these peaks could be given since they could also derive from atomic states of the adatom. The similarities of these peaks with the surface state band edge peak presented here, where we provide a clear assignment, suggest that the surface state localization is the origin of these peaks as well. We also suggest that band edge peaks observed at steps [32,33] and atomic lines [34] derive from the same localization phenomenon.

In conclusion, we have carried out STS experiments and simulations for a single Cu adatom on Cu(111). The simulations were based on a parameter-free wave packet propagation technique using density functional calculations to describe the perturbation introduced in the LDOS by the adatom. We have identified an electron resonance just below the surface state band edge that can be assigned to localization of the surface state at the adatom. The other resonances in the LDOS spectrum could be assigned to d_{z^2} and sp_z atomic orbitals of the adatom. The localization of the surface state is a direct consequence of the 2D nature of the surface state and of the attractive character of the Cu adatom. Hence, it is not specific to the present system and should appear in a variety of systems. Finally, we stress the important role of adatom-induced resonances, such as localization derived resonances, in excited state dynamics at surfaces [35], whereby such resonances are potential actors in chemical reactions at surfaces.

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