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Spectroscopy of an atom between two electrodes

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The electronic structure induced by an atom between two metal electrodes is probed by adsorbing atoms on a Ag(111) surface and contacting them with the tip of a scanning-tunneling microscope. Spectra of the differential conductance exhibit distinct structure and are different from spectra recorded at tunneling distances. A single-particle Newns-Anderson-type model reproduces the experimental line shape. The coupling of the adsorbed atom to the atom at the apex of the tip electrode induces an additional bond, which shifts and broadens the spectral features of the unperturbed atom-substrate system.

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Contacts of atomic dimensions exhibit properties which differ significantly from the familiar behavior of macroscopic conductors.[1–11] Experimentally, these properties have been explored using scanning-tunneling microscopy (STM),[1,2,5,6] point-contact spectroscopy,[3] and mechanically controlled break junctions.[4] These techniques enable spectroscopic measurement of the junction current versus bias voltage. Low-energy excitations such as Andreev reflections in the energy gap of superconductors,[3,12,13] phonon modes,[14] and the Kondo effect[9] have been explored. Electron transport, including inelastic-scattering effects, has been described on the basis of density-functional methods.[15–17] Experiments addressing the electronic structure of the contacts of a single atom or molecule at more elevated energies are scarce. Using the mechanically controlled break junction, current-voltage characteristics of conjugated organic molecules have been reported for voltage between −1 and 1 V.[18] Contact spectroscopy using STM has been performed in a voltage interval between −0.6 and 0.6 V to measure the spectroscopic signature of molecular orbitals of C_{60}.[19]

Here we report spectra of electronic excitations in single-atom contacts in an energy range up to 0.15 eV below the Fermi level. We take advantage of the capability of STM to probe the environment of an atom on a surface and obtain reproducible data for single atoms on extended atomically flat terraces. As a model case, we consider the (111) surface of Ag which exhibits interesting electronic structure not too far from the Fermi energy owing to its surface state. On this surface, adsorbed atoms (adatoms) are known to exhibit a well-defined resonance owing to surface-state localization.[20–23] Spectra recorded at different tip-sample separations up to the contact regime reveal a distinct variation. This variation can be reproduced within a single-particle Newns-Anderson-type model for the adatom and the tip apex atom. Bonding of the tip atom to the adatom broadens the resonance and causes splitting into bonding and antibonding adsorbate states.

The experiments were performed with a scanning-tunneling microscope operated at 7 K and in ultrahigh vacuum with a base pressure of 10^{-9} Pa. Sample surfaces and tungsten tips were cleaned by argon-ion bombardment and annealing. Silver atoms were produced by controlled tip-surface contacts,[8] while cobalt atoms were deposited with an electron-beam evaporator using a Co evaporant of 99.99% purity. Spectra of the differential conductance (dI/dV) were acquired with a lock-in technique using a modulation amplitude of 1 mV_{rms} and frequency of 10 kHz. Various tip-adatom distances were set by operating the microscope at different currents before opening the feedback and freezing the tip position. The contact area was imaged prior to and after spectroscopic measurements to verify the geometry and integrity of the contact.

Figures 1(a) and 1(b) display spectra of dI/dV recorded at contact, which is formed between tip and atom at a current of $I \approx 12$ μA and a voltage of $V = -0.2$ V [see circle in Fig. 2(a)] and thus at a contact conductance of $I/V \approx 0.8 G_0$ ($G_0 = 2e^2/h$, $-e$ is the electron charge, and h is Planck's constant).[8,24] They exhibit an indentation close to the binding energy of the Ag(111) surface state ($\varepsilon_s = -0.067$ eV) and are asymmetric with respect to this energy. Moreover, essentially

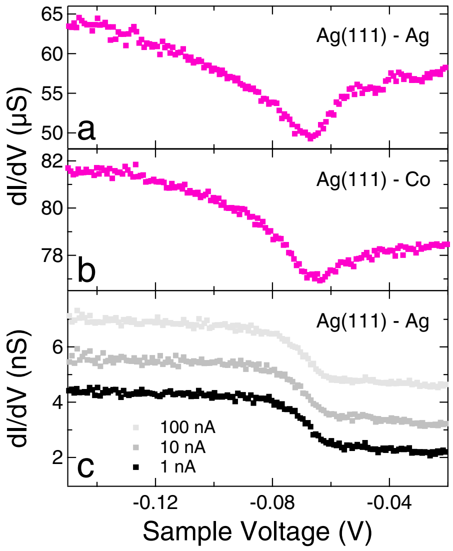

FIG. 1. (Color online) (a) and (b) Contact spectra of the differential conductance (dI/dV) of single Ag and Co adatoms. Tunneling gaps were set at −0.2 V, 12.3 μA for Ag(111)-Ag and at −0.16 V, 12.7 μA for Ag(111)-Co. (c) dI/dV spectra acquired with the tip above a single Ag adatom at various tip-adatom distances (tunneling gap parameters: −0.2 V and indicated tunneling currents). Spectroscopic data acquired at 10 and 100 nA were scaled by factors of 0.1 and 0.01 and shifted vertically by −1 and −2 nS.

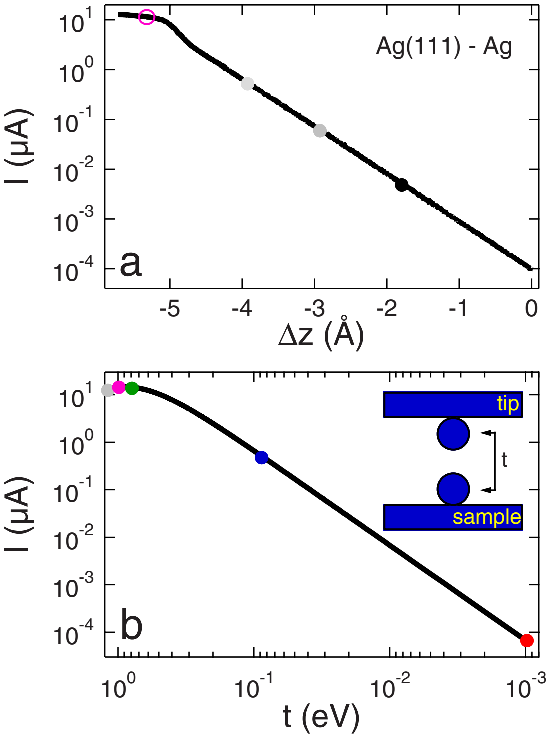

FIG. 2. (Color online) (a) Current I versus displacement Δz of the tip approaching a single Ag adatom. Zero displacement is defined by tunneling parameters prior to opening the feedback loop (−0.2 V, 0.1 nA). Dots indicate the currents for tunneling spectra of dI/dV shown in Fig. 1(c). A circle indicates the contact current for spectra shown in Figs. 1(a) and 1(b). (b) Calculated current as a function of coupling parameter t for a sample voltage of $V = -0.2$ V. Dots indicate the current and coupling parameter for the calculated differential conductance in Fig. 3. Inset: Illustration of setup used for calculations.

identical characteristics are observed for Ag and Co, indicating that the spectral structure is not directly linked to the chemical nature of the adatoms.

It is useful to compare the contact spectra with reference data recorded at tunneling distances [Fig. 1(c)]. The reference spectra exhibit the typical signature of surface-state localization.[20–23] The conductance is increased at sample voltages $V < -0.06$ V, which correspond to energies near and below the surface-state band edge. Within the tunneling range the shape of these spectra is independent of the tip-adatom distance. As the current varies significantly over this range, the absence of broadening indicates that no significant heating of the junction occurs at elevated currents.

The conductance spectrum at contact is strongly modified by the interaction of the electronic states of the sample with the tip apex atom. In particular, the spectral structure is broadened and its relative amplitude is reduced. In the tunneling regime the localized state leads to a conductance variation by ≈100%, while at contact the variation in the conductance is less than 10%.

To interpret the spectra at contact we start from the Newns-Anderson-type single-particle model introduced in Ref. 22. As an extension to this model we take the tip atom explicitly into account and model it by a single Ag atom on a silver substrate [inset of Fig. 2(b)]. This tip apex atom is described by a single s state $|a,\text{tip}\rangle$ with energy ε_a, which couples to tip bulk states with energies $\varepsilon_{\mathbf{k}}$ via transfer-matrix elements $v_{a\mathbf{k}}$. The tips used in the experiments appear to be terminated by a single atom and thus do not exhibit a surface state. We therefore solely consider coupling of the atomic s state to tip bulk states. In particular, the relevant parameters are assumed to be the same as for the Ag(111)-Ag adsorbate system described in Ref. 22 and below. The Hamiltonian matrix describing the tip is

$$H_{\text{tip}} = \begin{pmatrix} \varepsilon_{\mathbf{k}} + |e|V & v^{\dagger}_{a\mathbf{k}} \\ v_{a\mathbf{k}} & \varepsilon_a + |e|V \end{pmatrix}. \tag{1}$$

For the adatom-substrate system we have[22]

$$H_{\text{sample}} = \begin{pmatrix} \varepsilon_a & v_{a\mathbf{k}} & \tilde{v}_{a\tilde{\mathbf{k}}} \\ v^{\dagger}_{a\mathbf{k}} & \varepsilon_{\mathbf{k}} & 0 \\ \tilde{v}^{\dagger}_{a\tilde{\mathbf{k}}} & 0 & \tilde{\varepsilon}_{\tilde{\mathbf{k}}} \end{pmatrix}. \tag{2}$$

The Ag adatom on Ag(111) is likewise described by a single s orbital, which couples to Ag bulk states and additionally to the Ag(111) surface state with energy $\tilde{\varepsilon}_{\tilde{\mathbf{k}}}$ via transfer-matrix elements $\tilde{v}_{a\tilde{\mathbf{k}}}$.

The coupling of the adsorbate state to the bulk states results in a self-energy of the form $\Sigma_b = \Lambda_b - i\Delta_b$, and the coupling to the surface state to a self-energy $\Sigma_s(\varepsilon) = \Lambda_s + \pi^{-1}\Delta_s \ln|\varepsilon - \varepsilon_s| - i\Delta_s \Theta(\varepsilon - \varepsilon_s)$, where the Heaviside step function Θ describes the surface-state onset. Within this simple model for the adsorbate system alone a constant real part of the self-energy can be absorbed in ε_a, and for simplicity we assume $\Lambda_b = 0$ and $\Lambda_s = 0$ in the following. While the surface-state band edge was used as energy reference in Ref. 22, we consider ε_s explicitly here and use the Fermi energy ε_F as energy reference instead. The other parameters are taken from Ref. 22; i.e., $\varepsilon_a = 0.5\ \text{eV} + \varepsilon_s$, $\Delta_b = 0.8$ eV, $\Delta_s = 0.5$ eV, and ε is measured in eV. In that work these parameters were derived by a fit of the projected density of states at the Ag adatom to observed tunneling spectra.

A recent study of the size-dependent electronic structure of silver clusters on Ag(111) reported a p_z-like Ag monomer resonance at ≈3 eV above the Fermi level and with a full width at half maximum of ≈1 eV.[25] It is tempting to set the adsorbate level ε_a to this resonance energy. However, since the energy of the resonance is considerably larger than the surface-state binding energy and the resonance width is rather narrow, the coupling of the resonance to the surface state is most likely very weak. Therefore, we resort to $\varepsilon_a = 0.5\ \text{eV} + \varepsilon_s$ which is the energy of a broad s-like resonance exhibiting appreciable overlap with the surface-state band. Assigning predominantly s character to the adatom-induced localized state is in agreement with recent *ab initio* studies of 3d impurities on Cu(111).[23,26]

The interaction between the tip atom and the adatom is described by a transfer energy t. The Hamiltonian of the complete system then reads

$$H = \begin{pmatrix} H_{\text{tip}} & T \\ T^{\dagger} & H_{\text{sample}} \end{pmatrix}. \tag{3}$$

The only nonvanishing matrix element of the coupling matrix T refers to the direct interaction between the atomic s orbital of the tip and the adatom, $\langle a,\text{tip}|T|a,\text{sample}\rangle = t$.

A similar model system of two adsorbate atoms connected to reservoirs and interacting via a transfer-matrix element t was discussed by Frederiksen *et al.*[27] in addition to their density-functional-theory (DFT) calculations to model the crossover from tunneling to contact in Au junctions. Our considerations extend that model by including the coupling of the Ag adatom not only to Ag bulk states but also to the Ag(111) surface state, which is essential for the occurrence of the localized state split off from the surface-state continuum.

The current I from sample to tip is given by a Landauer-Büttiker-type expression (Refs. 28–31 and references therein). Including a factor of 2 to account for spin degeneracy, we obtain for the elastic current

$$I = \frac{8|e|}{h}|t|^2 \int_{\varepsilon_F}^{\varepsilon_F+|e|V} d\varepsilon \times \frac{\text{Im}(\Sigma_b)\text{Im}[\Sigma_b + \Sigma_s(\varepsilon)]}{|(\varepsilon - \varepsilon_a - |e|V - \Sigma_b)[\varepsilon - \varepsilon_a - \Sigma_b - \Sigma_s(\varepsilon)] - |t|^2|^2}. \tag{4}$$

The current as a function of coupling parameter is shown in Fig. 2(b) for a fixed sample voltage of $V = -0.2$ V. The coupling parameter is expected to decrease exponentially with tip-sample separation. If we identify the contact region by the interval of coupling energies where I deviates from the $I \propto |t|^2$ tunneling behavior, we conclude from Fig. 2(b) that contact corresponds to $t = \mathcal{O}(1\ \text{eV})$. Results for the differential conductance are shown in Fig. 3 for a range of interaction parameters t close to and at contact. While the tunneling spectra basically display a steep and significant increase in the differential conductance below ε_s due to the localized state split off from the surface state by the adsorbate,[21,22] the step appears broadened at contact and the step height decreases. This mimics the experimental observations. As the theoretical model contains several simplifications, e.g., the density of states of the tip atom is described by a single s resonance and the Ag(111) surface-state density of states is modeled by a step function, no improvement of the fit to the experimental data was attempted. Nevertheless, we conclude that two mechanisms may yield a modification of the projected density of states at the Ag adatom, and thereby induce changes in the spectra. First, the coupling to the tip atom results in the opening of additional decay channels for the adsorbate state and an increase in the imaginary part of the self-energy. Second, the interaction between tip and adsorbate atom causes a splitting into bonding and antibonding states, which distinctly modifies the projected density of states, in particular when the energy of the bonding state shifts below the band edge of the surface state at ε_s and thus determines the shape of the spectrum in the energy range below ε_s.

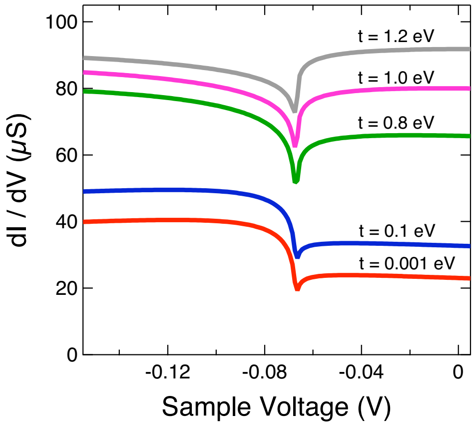

FIG. 3. (Color online) Calculated differential conductance versus sample voltage for values of the coupling constant below ($t = 0.001$ eV and $t = 0.1$ eV) and at contact ($t = 0.8$ eV, $t = 1.0$ eV, and $t = 1.2$ eV). The distinct differences between tunneling and contact spectra observed in experimental data (Fig. 1) are reproduced. To plot curves on a common axis, data for $t = 0.001$ eV and $t = 0.1$ eV have been multiplied by 10^5 and 10, respectively. Data for $t = 0.1$, 1.0, and 1.2 eV have additionally been offset vertically by 10, 8, and 20 μS, respectively.

Our model likewise predicts the reduced magnitude of the overall conductance variation which is observed in the experiments. At contact ($t = 0.8$ eV), the modeled variation in the differential conductance is ≈20% over the plotted voltage interval (without considering the dip close to ε_s). This reduction is due to the bonding state of the dimer formed by the tip apex atom and the adatom which shifts below the Ag(111) surface-state energy. Moreover we suggest that further states not considered in our model may contribute to the conductance at contact, which may result in an additional background that is only slowly varying with energy. As a result, the variations due to the adatom are less prominent than in conventional tunneling spectra at larger tip-adatom distances.

In summary, single Ag or Co adatoms on a Ag(111) surface are known to give rise to a localized resonance just below the surface-state band edge. Spectroscopy of dI/dV of the adatom at contact with the tip of a scanning-tunneling microscope results in a line shape that characteristically differs from the spectra observed in the tunneling regime. A Newns-Anderson-type single-particle model reproduces the observed qualitative variations in the resonance line shape. The model accounts for the increased number of bulk states available for decay at contact, and the change in the projected density of states caused by the splitting of the adatom and tip states into bonding and antibonding states due to the tip-adatom interaction.

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