Empty Valence-Band Pocket in p-Type Cu$_2$O(111) Probed with Scanning Tunneling Spectroscopy

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Scanning tunneling spectroscopy is used to probe the surface electronic structure of ($\sqrt{3} \times \sqrt{3}$)-reconstructed cuprous oxide films on Au(111). In analogy to bulk Cu$_2$O(111), the films show a pronounced p-type nature with the valence-band top pinned to the Fermi level and the conduction-band onset located at +2.0 V. A conductance dip appears directly at zero bias in the d$I$/d$V$ spectra, followed by an asymmetric d$I$/d$V$ maximum inside the lower half of the bandgap. Several scenarios are considered to explain this unusual conductance behavior. The most likely interpretation is based on the accumulation of hole states in the p-type material in response to the tip-electric field and the development of an empty valence-band pocket directly below the tip. Tunneling into these states leads to a finite d$I$/d$V$ intensity even inside the Cu$_2$O bandgap. A 1D tunneling model that accounts for this field-dependent transport mechanism successfully reproduces the experimental data and rationalizes the impact of current setpoint, oxide thickness, and surface reconstruction on the observed spectral response.

1. Introduction

Differential conductance (d$I$/d$V$) spectroscopy with a scanning tunneling microscope (STM) is an established tool to probe the surface electronic structure at atomic length scales. A large number of fascinating experiments have been realized in past years, addressing surface states and their spatial confinement, the nature of molecular orbitals, defect and impurity levels in dielectrics, quantum-well states in metal particles, and much more.

Additional insights are available when reading other spectroscopic channels, for example, the second harmonics of the tunneling current to identify molecular vibrations, the photon response for nanoscale optical analyses, and spin-sensitive signals to probe surface magnetism. With this impressive spectroscopic toolbox, the STM remains one of the most versatile techniques to explore the quantum structure of matter. However, interpretation of STM conductance data remains challenging even after 35 years of experience. One reason is the ambiguity of d$I$/d$V$ traces that essentially probe the energy-dependent decay of wave functions above the surface by means of poorly defined tips. Other parameters, such as the wave vector or the elemental nature of the electronic states, are not accessible. Moreover, certain states are not detected at all, as their localization in the surface inhibits sufficient wave function overlap with the tip. STM spectroscopy is thus susceptible to misinterpretations, for instance, if relevant conductance channels are neglected and faulty model structures or electron transport pictures are used. Examples are Coulomb charging of metal particles that was confused with the density of states (DOS), inelastic tunneling into vibrational modes that was erroneously related to Kondo physics, and bandgaps of dielectric materials that were not corrected for band-bending effects in the tip-electric field. Also, a nonmonotonous state density of the tip or the presence of multiple tunneling paths may lead to faulty interpretation of d$I$/d$V$ spectra.

This article discusses “unusual” STM conductance spectra measured on cuprous oxide (Cu$_2$O) films grown on Au(111). Our data provide insights into the electronic structure of this fascinating material, but also bear the risk of misinterpretations. Cuprous oxide is one of the few p-type conductive oxides and expected to play a central role in the development of all-oxide electronic devices. Its p-type conductivity originates from a thermodynamic preference for Cu vacancies in the lattice, which in turn generate robust electron acceptors at the valence-band top. Their energy positions have been calculated with density functional theory (DFT) but were never experimentally confirmed and conflicting information exists in the literature. Other electronic peculiarities are associated with copper oxides, for example, exceptionally large binding energies for excitons and unconventional superconductivity emerging in doped Cu–O planes.

We recently developed a new experimental route to grow Cu$_2$O films via high-pressure Cu oxidation. The good quality of our samples combined with state-of-the-art DFT calculations gave rise to a new structure model for the long-known ($\sqrt{3} \times \sqrt{3}$) R30º reconstruction of Cu$_2$O(111). It is based on Cu$_2$O nanopyramids located at every third Cu–O six ring of the bulk-cut...
surface. In this work, STM conductance spectra of the Cu$_2$O(111) surface are presented that confirm the expected p-type nature of the material with the Fermi level ($E_F$) pinned directly at the valence-band top. Moreover, a series of d$I$/d$V$ maxima is detected inside the bandgap, suggesting the presence of Cu vacancies in the lattice. Although such an interpretation would be in accordance with DFT calculations, we offer an alternative model in which the in-gap intensity originates from an empty-state pocket at the valence-band top that forms in the tip-electric field. Our work thus demonstrates once more the caution that has to be exercised in the interpretation of STM conductance data.

2. Results

The Cu$_2$O films grown for our experiments exhibit a granular texture with grains of 50–100 nm diameter and 1–3 nm height (Figure 1a). The crystallites are characterized by flat top facets with (111) termination, as concluded from low-energy electron diffraction (LEED) (Figure 1a, inset). At the atomic scale, the surface is homogeneously covered with a hexagonal network of trifold symmetric protrusions of 0.15 nm height and 1.05 nm periodicity (Figure 1b). The latter matches the ($\sqrt{3} \times \sqrt{3}$)R30° superstructure seen in LEED and corresponds to the nanopyramidal reconstruction devised by DFT.[20] It is composed of Cu$_4$O units, in the following referred to as shamrocks, bound to every third Cu–O six ring in the surface (Figure 1c). The rings next to the nanopyramids are empty and even lack the low-coordinated Cu$_{cu}$ atoms that would terminate a bulk-cut (111) surface. The reconstruction is slightly Cu deficient and removes all O$_{cu}$ dangling bond states apart from the ones of the capping O ions of the pyramids. This results in a substantial stabilization of the Cu$_2$O(111) surface and renders the reconstruction thermodynamically preferred in a wide range of oxygen chemical potentials.[20,21]

Insight into the electronic properties of the reconstructed Cu$_2$O(111) surface is obtained from d$I$/d$V$ spectroscopy (Figure 2a). The spectra are governed by a pronounced gap region, extending from zero to +2.0 V sample bias. The asymmetry with respect to $E_F$ reflects the p-type conductance behavior of Cu$_2$O and suggests an abundance of Cu vacancies in the oxide matrix.[15,16] The p-type response is robust and prevails even in Cu$_2$O nanocrystallites that develop in a dewetting transition at temperatures above 700 K.[19] Interestingly, the d$I}$/d$V$ signal does not vanish completely inside the bandgap but exhibits a characteristic fine structure that is best seen on a logarithmic scale (Figure 2b). When reaching the valence-band edge, the d$I$/d$V$ signal sharply drops to zero but quickly recovers to a finite value above the Fermi level. The intensity then exhibits

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**Figure 1.** a) STM overview ($U_A = 1.5$ V, $I = 50$ pA, $120 \times 120$ nm$^2$) and b) zoom-in image ($14 \times 14$ nm$^2$) of Cu$_2$O films on Au(111) prepared in 50 mbar O$_2$. c) The surface is homogenously covered with shamrock units, bound to every third Cu–O six ring ($3 \times 3$ nm$^2$). d) A ball model of the reconstructed Cu$_2$O(111) surface as derived from DFT calculations.[20] The LEED pattern in the inset of (a) shows the fundamental ($1 \times 1$) spots and the ($\sqrt{3} \times \sqrt{3}$) reconstruction of the surface.

**Figure 2.** STM conductance spectra acquired on thick (upper three spectra) and thin (lower four spectra) Cu$_2$O grains, plotted on a) linear and b) logarithmic scale. The histogram shows peak energies that are obtained when deconvoluting the in-gap intensity into two Gaussians of identical width. c) Spectral series acquired on Cu$_2$O(111) as a function of the tunneling current. d) Spectra measured on Cu$_2$O regions with A) low and B) high density of shamrocks. The corresponding spectral positions are marked in the STM image shown in the inset ($13.5 \times 9.5$ nm$^2$). All spectra are offset for clarity and measured with the same bias setpoint of 2.5 V.
a broad and asymmetric course that extends over the lower half of
the gap up to \( \approx 1.0 \) V. Directly at zero bias, a symmetric conduc-
tance dip of \( \approx 100 \) mV width shows up, which separates the actual
band edge from the in-gap intensity. The negative side of this dip
is delimited by a distinct kink at \(-250\) mV, below which the \( dI/
dV \) signal rises less steeply (see arrow in Figure 2b). The upper
half of the Cu\(_2\)O gap region is featureless until the conduc-
tance dip of \( \approx 1.0 \) V.

To gain further insight into the distinct zero-bias minimum,
we acquired current-dependent conductance spectra, as shown in
Figure 2c. Upon increasing the current from 0.1 to 2 nA, the in-
gap intensity continuously rises and the zero-bias dip becomes
more pronounced. The overall spectral shape does, however, not
change with the setpoint conditions. A second spectral series
addresses the role of the local shamrock density on the Cu\(_2\)O
surface (Figure 2d). Apparently, the in-gap maximum is more
confined to low bias if the shamrock concentration is high
(region B) but broadens toward higher energies on open
Cu\(_2\)O patches (region A). The asymmetry of the in-gap intensity,
governed by a steep rise at \( E_F \) and a slow decline at higher bias, is
revealed however throughout the oxide surface.

The shamrock units themselves do not leave a \( dI/dV \) finger-
print in the oxide bandgap. This is concluded from \( dI/dV \) spectra
taken directly on the shamrock positions, but also from conduc-
tance maps acquired at bias voltages inside the gap. The latter
display no \( dI/dV \) intensity related to the shamrock maxima, even
if they are well resolved in the topographic channel (Figure 3).
Only close to the band edges, the shamrocks develop measurable
\( dI/dV \) signals and appear as simple protrusions close to the
valence-band top but with distinct sombrero contrast, that is, a
dark ring surrounding a bright center, at the conduction-band
onset. The following section aims at correlating the characteristic
conductance behavior observed on the Cu\(_2\)O(111) surface with
the oxide electronic structure.

3. Discussion

Zero-bias anomalies in the differential conductance often provide
a hint at interesting physics, such as Kondo effects due to
magnetic impurities,[13] Coulomb-blockade phenomena,[22]
and minigaps in topological insulators and superconductors.[21,24]
Most of these phenomena can be discarded for a non-
magnetic, dielectric oxide and an experimental temperature of
about 100 K. However, three options should be examined in
detail, namely, polaronic charge transport, defect states
in the Cu\(_2\)O gap, and tip-induced band-bending effects.
Polaronic charge transport occurs in many dielectric systems
if electrons/holes are temporarily trapped at structural defects
and self-sparked lattice distortions on their way through the crys-
tal.[25,26] To move a carrier from one to the next lattice site, this
trapping potential has to be overcome or the polaronic distortion
defines together with the charge.[27,28] The resulting
hopping transport gives rise to an Arrhenius-type temperature
dependence of the current: \( I \sim \exp \left( \frac{-E_f}{k_B T} \right) \) with \( E_f \) the activation
energy.[29] Cu\(_2\)O is known for polaronic charge transport,[30,31]
whereby the confining potential is associated with Cu defects
in the lattice.[16,17] In a possible first scenario, the zero-bias
anomaly might thus be related to such a hopping behavior.
The associated transport barrier could then be reduced by the
tip-electric field, which enables electron transport even at low
temperature. As a finite-bias threshold is required to beat the
hopping potential, a distinct conductance dip is expected to
develop directly at \( E_F \). In certain aspects, this mechanism resembles
the Cabrera–Mott scheme for metal oxidation, where local
electric fields lower the barrier for diffusive mass transport[32]

Although the experimental half width of the zero-bias dip
(50 meV) agrees well with reported Cu\(_2\)O hopping energies
(35–70 meV),[31,33] we discard this option for several reasons.
We have tested the impact of thermal activation on a possible
polaronic transport scheme by lowering the measuring tempera-
ture from 130 to 80 K. Within the experimental accuracy, no
changes could be detected in the zero-bias response of the sys-
tem. In addition, the tip-electric field was varied by changing the
tunneling current by one order of magnitude (Figure 2c).
Whereas the positive side of the \( dI/dV \) dip showed rising inten-
sity at higher current, hardly any changes were detected at the
negative side, rendering the results nonconclusive. Finally,
polaronic charge transport typically provokes another signature in
STM spectroscopy, namely, pronounced \( dI/dV \) oscillations
around sharp conductance steps. These bias modulations are
caused by optical phonons that typically contribute to the trap-
ning/releasing of carriers in polaronic transport. Respective
\( dI/dV \) oscillations were previously detected around ZnO impu-
rities levels and at the onset of the CaO conduction band,[34,35] yet
not in the present study on Cu\(_2\)O. We thus consider polaronic
charge transport to be an unlikely reason for the zero-bias dip.
A second explanation for the in-gap dI/dV intensity concerns resonant tunneling into localized gap states of cuprous oxide. As stated earlier, the p-type conductance of Cu$_2$O relies on low-lying acceptor levels introduced by Cu vacancies in the lattice.\cite{16,17} The gap states were proposed to lie in an energy window of 0.15–0.65 eV above the valence-band top, based on deep-level transient spectroscopy and photo-luminescence data.\cite{18,31,36,37} Further insights were provided by DFT calculations that found two kinds of Cu defects to be stable in Cu$_2$O.\cite{38,39,40} The first one, referred to as simple vacancy, is formed by removing a Cu atom from the lattice and leaves behind two low-coordinated O$_{\text{CuS}}$ ions. In the split vacancy, in contrast, a neighboring Cu moves toward the defect position until it reaches tetrahedral coordination with four adjacent O ions. While the structural parameters seem settled for the two defect types, the energy of the associated gap states varies substantially with the level of approximation. While gradient-corrected DFT methods predict defect energies that are inconsistent with experimental data,\cite{17} hybrid DFT approaches find both vacancy types to lie within 1.0 eV above the valence band with the simple vacancy being thermodynamically preferred.\cite{39,40}

The asymmetric dI/dV traces detected within the Cu$_2$O bandgap would be in line with the presence of two distinct defect states. In fact, most of the conductance spectra could be fit with two Gaussians of $\sim0.25$ V width, being preferentially centered at 0.4 and 0.75 V (see inset of Figure 2a). These bias values agree fairly well with the most reliable level energies calculated for the simple and split vacancy, respectively.\cite{39,40} Despite this correspondence, we hesitate to assign the in-gap dI/dV intensity to resonant tunneling into Cu vacancy states for good reasons. First, the characteristic dI/dV response is detected everywhere on the Cu$_2$O surface, with some variations in the intensity but not in the relative weight of the two maxima. Assuming a dI/dV response due to the superposition of two defect levels, we would expect a larger spatial inhomogeneity of the spectral shape. Second, no structural defects could be identified in topographic and conductance images that would be compatible with a Cu vacancy. The shamrocks, as the most prominent structural peculiarity in the reconstructed Cu$_2$O surface, have been assigned to Cu$_2$O nanopyramids before, and even O$_{\text{CuS}}$ defects were unambiguously detected in our experimental data.\cite{20} An experimental signature of the Cu defects, on the other hand, was not revealed so far. Third, the observation of a sharp and symmetric conductance dip at zero bias seems incompatible with resonant tunneling into Cu defect states.

With these considerations in mind, we propose a third interpretation of the in-gap dI/dV intensity observed for Cu$_2$O(111) films. Starting point is again the p-type conductivity of the oxide with the valence-band edge pinned at $E_F$. Tunneling at small negative bias thus corresponds to electron transport out of filled valence states and gives rise to high dI/dV intensity (Figure 4a). The conductance decreases sharply when reaching the valence-band top directly at $E_F$. However, a new transport channel opens up at positive bias, as revealed by a sudden dI/dV intensity rise (Figure 2). This finding seems surprising at first glance, because the initial tip states only face the filled valence band and the gap region of Cu$_2$O. The required empty states for tunneling may develop, however, due to the interplay of the p-type oxide characteristics and the electric field exerted by the STM tip. Already at low positive bias, the Cu$_2$O valence band is lifted above $E_F$, enabling the hole gas related to the p-character to accumulate in an empty-state pocket at the valence-band top. The band bending proceeds until the local Fermi level, given by the hole concentration in the oxide region below the tip, is in balance with $E_F$ of the gold support (Figure 4b). The empty-state pocket now enables electron tunneling from the tip to the Cu$_2$O film and explains both, the appearance of a conductance dip at zero bias and the recovery of the dI/dV intensity inside the bandgap. The low in-gap signal hereby reflects the limited transport capacity of the new channel that is governed by the finite concentration of hole states at the valence-band top. With increasing bias, the dI/dV signal declines again, as the hole pocket remains pinned at $E_F$ and the tip electrons experience an increasing barrier for tunneling. With other words, the initial states in this unusual transport channel locate deeper and deeper below the Fermi level of the tip. The asymmetric dI/dV intensity detected in the Cu$_2$O(111) bandgap thus arises from electron tunneling into an empty valence-band pocket that declines as the associated barrier increases at higher bias.

To support the proposed transport mechanism, we have simulated the tunneling current across an STM junction made of Au tip and Cu$_2$O/Au(111) sample using the Wenzel–Kramers–Brillouin approximation:\cite{11} 

$$I \sim \int_{E_F}^{E_F+\Delta E} dE \cdot \rho_{\text{sample}}(E_{\text{Tip}}, E) \cdot \rho_{\text{Tip}}(E - eV) \cdot \delta(z, E).$$

The transmission coefficient is hereby defined as $T(z, E, V) = \exp(-\frac{\hbar}{2m} \sqrt{2m[\varphi - E + \frac{1}{2}eV]})$ with $z$, $V$, and $\varphi$ accounting for tip-sample distance, sample bias, and work function (set to 5.0 eV as mean value for Cu$_2$O and Au), respectively. While the density of tip states ($\rho_{\text{Tip}}$) is set constant, reflecting the flat
DOS of our gold tip, $\rho_{\text{Sample}}$ includes the Cu$_2$O valence band, the gap region, as well as tip-induced band-bending effects. The latter are approximated with the model of a plate capacitor filled with vacuum ($z = 0.5$ nm for tip-sample separation) and Cu$_2$O ($d = 1$–$3$ nm and permittivity $\varepsilon_r = 7.1$).\cite{41} The ratio of voltage drops in the vacuum and the dielectric film then calculates to $\eta = \frac{V}{z}$.\cite{42} In the experimental Cu$_2$O thickness range, 5–30% of the applied bias drops inside the oxide film and causes the valence band to bend upward with respect to the nonbiased junction. The results of our simulations are shown in Figure 4c,d for different current setpoints and bending effects, respectively. In both cases, high conductance values are obtained at negative bias due to effective tunneling out of the filled Cu$_2$O valence band. The conductance drops to zero when reaching the band edge at $E_F$, but quickly recovers at small positive bias due to electron tunneling into the hole pocket that forms at the valence-band top. With increasing positive bias, the conductance saturates and decreases again, reflecting the rising barrier height and the reduced transmission coefficient in the above equation. Our simulations therefore qualitatively reproduce the experimental data, in particular what the asymmetry of the in-gap $dI/dV$ response concerns. No quantitative match can be expected because of the unknown hole concentration in the Cu$_2$O films and uncertainties in the DOS at the band edges.

Our simulations also predict an in-gap conductance that increases with setpoint current due to the higher tunneling probability at smaller tip-sample distance (Figure 4c). Moreover, the maximum in the $dI/dV$ traces shifts to higher bias, in line with the experimental data. In turn, stronger band bending in thicker films leads to a larger hole pocket at the valence-band top and provides more final states for tunneling electrons. The result is an increasing in-gap conductance, and higher $dI/dV$ intensities are indeed observed for thicker Cu$_2$O patches (Figure 2a). Also, the different conductance behavior measured on top of the shamrock reconstruction as compared with small open Cu$_2$O(111) areas is covered by our model (Figure 2d). The shamrock maxima, being identified as Cu-rich nanoprisms by means of DFT,\cite{20} allow for a better screening of the tip-electric field and hence reduced band-bending effects with respect to the pristine surface. Smaller band bending now implies lower in-gap conductance, as indeed detected in oxide regions with high shamrock concentration (Figures 2d and 3). Conclusively, our model seems suited to reproduce the asymmetric $dI/dV$ traces detected in the gap region of Cu$_2$O films.

5. Experimental Section

The experiments were conducted with a custom-built STM operated at liquid nitrogen temperature. The instrument was embedded in an ultra-high-vacuum chamber ($p = 2 \times 10^{-10}$ mbar), equipped with standard surface-science tools for sample preparation and analysis and a high-pressure cell. STM imaging was done at the constant current mode with electrochemically etched gold tips. Differential conductance ($dI/dV$) spectra were acquired with lock-in technique at 14 mV modulation bias and $\approx 1800$ Hz. The Cu$_2$O films were grown by depositing $\approx 10$ monolayers of copper onto a sputtered/annealed Au(111) surface, followed by a high-pressure oxidation step in 50 mbar O$_2$ at 450 K. To prevent uncontrolled reduction, the samples were postannealed at 650 K in front of an oxygen nozzle at $10^{-4}$ mbar local pressure. Photoelectron spectroscopy measurements verified the oxide stoichiometry to be Cu$_2$O.\cite{49}

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

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