

Emergence of surface states in nanoscale Cu₂N islands

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We studied electronic states in nanoscale Cu₂N islands on Cu(100) using scanning tunneling microscopy and density functional theory. Tunneling spectra indicate a state at ~ 2 V in large islands (> 20 nm²), which shifts due to quantum confinement in smaller islands. This state is not observed for islands with fewer than ~ 50 atoms. In contrast, a 4 V state persists down to 12 atom islands, but it does not shift within experimental error. Theory suggests that these differences reflect the different effective masses of the two Cu₂N bands, as well as their coupling to a Cu surface state.

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The bulk electronic band structure of solids first emerges from atomic orbitals in nanoscale clusters. The scanning tunneling microscope (STM) is a useful tool for studying the properties of nanoclusters on surfaces ranging in size from 1 to $> 10^4$ atoms. Tunneling spectroscopy can probe the valence orbitals of single adatoms¹ and the evolution of quantum confinement in atomic chains² or adatom islands^{3,4} on metal surfaces. Recently, there has been considerable interest in isolating such structures from the metal surface by using an intervening, few-monolayer-thick insulating film (e.g., Cu₂N, NaCl, Al₂O₃, MgO).⁵⁻⁷ Ultrathin insulating films are themselves a form of nanocluster; prior studies have shown that a bulk-like band gap is already established in few-layer NaCl⁸ and MgO films.⁹ While these studies probed the influence of quantum confinement in one dimension down to the nanometer scale, the lateral sizes of such films were too large to see additional confinement effects.

Here, we study the emergence of electronic states in one-atomic-layer-thick Cu₂N films, ranging in lateral area from quasi-continuous monolayers to sub-nm² islands. STM measurements reveal the quantum-confined blueshift of an unoccupied state with decreasing island area down to ~ 1.5 nm², corresponding to ~ 50 atoms. While similar quantum-confined energy shifts have been observed in a variety of STM studies,⁴ our studies extend down to smaller islands (0.5 nm² or 12 atoms), where the state itself is no longer observed. This trend is qualitatively reproduced in our density functional theory (DFT) calculations of the local density of states (LDOS). In contrast, a higher-energy state exhibits no systematic shift with area and persists down to the smallest islands studied. Our DFT calculations suggest that this contrasting behavior reflects the different effective masses of the two Cu₂N bands, and their proximity in energy to a Cu surface state.

Films of Cu₂N were grown by sputter deposition of atomic N onto a clean Cu(100) surface, followed by annealing at 350° C.¹⁰ Mobility during annealing facilitates the self-assembly of nitrogen atoms into islands with a (2×2) periodicity (i.e., N adsorbs in every other hollow site).¹¹ We varied island size and shape by adjusting nitrogen coverage and annealing time. Low nitrogen coverage and short annealing time (~ 30 s) lead to small, irregularly shaped islands. Increased annealing time (~ 2 min) makes the islands squarer, while increased nitrogen coverage forms islands up to

$\sim 5 \times 5$ nm².¹¹ These islands coalesce into quasi-continuous monolayer films with further coverage.¹²

All measurements were made with a Createc STM operating at a base temperature of 5.3 K in ultrahigh vacuum ($< 1 \times 10^{-10}$ mbar). All data shown here were collected using a cut Ir tip. We studied Cu₂N islands with three modes of tunneling spectroscopy.¹⁰ In “constant height” mode, the STM feedback was turned off, and the tunnel current was recorded as a function of voltage, $I(V)$. By adding a 5 mV_{pp} modulation at 855 Hz to the voltage, a lock-in amplifier was able to measure the differential conductance, dI/dV . At low voltage (i.e., $< |1V|$), dI/dV is approximately proportional to the joint LDOS of tip and sample.^{13,14} We also measured dI/dV while varying both voltage and tip height (“z-ramp” mode) or while the feedback remained active (“constant current” mode). These two modes were useful for monitoring the joint LDOS over a larger voltage range, although dI/dV was no longer simply proportional to the LDOS. Spatial maps of dI/dV at fixed voltage were obtained by recording the lock-in signal as the tip was scanned across the surface with feedback on.

DFT calculations were performed using the projector augmented wave (PAW) method.^{15,16} A Perdew-Burke-Ernzerhof (PBE) exchange correlation functional was used with the generalized gradient approximation (GGA),¹⁷ as implemented in the Vienna ab-initio simulation package (VASP).^{18,19} We studied a monolayer film of Cu₂N, as well as 12 atom (Cu₈N₄) and 48 atom (Cu₃₂N₁₆) islands, all on Cu(100). We spaced islands from their periodic images by two bulk Cu lattice constants (7.2 Å). The unit cell consisted of a symmetric slab of seven Cu layers, with N adsorbed on both faces to prevent unphysical multipoles, and a vacuum region of thickness equal to the Cu slab. We used unrelaxed structures, but based on experiment,²⁰ we introduced a 4% vertical expansion of the outer Cu layer, with N atoms 0.4 Å above hollow sites. More intensive computations with relaxed structures, larger interisland spacing (i.e., three Cu lattice constants instead of two), or thicker Cu slabs (i.e., nine Cu layers) yielded qualitatively similar results. Numerical convergence of total energy to ~ 10 meV for vacuum thickness of the monolayer unit cell and k -points for the islands was achieved, and a 550 eV plane wave cutoff energy was used.

For more accurate comparison with scanning tunneling spectroscopy, which typically probes states near the Γ point,^{13,14} we calculated LDOS by using a $9 \times 9 \times 1$ mesh of

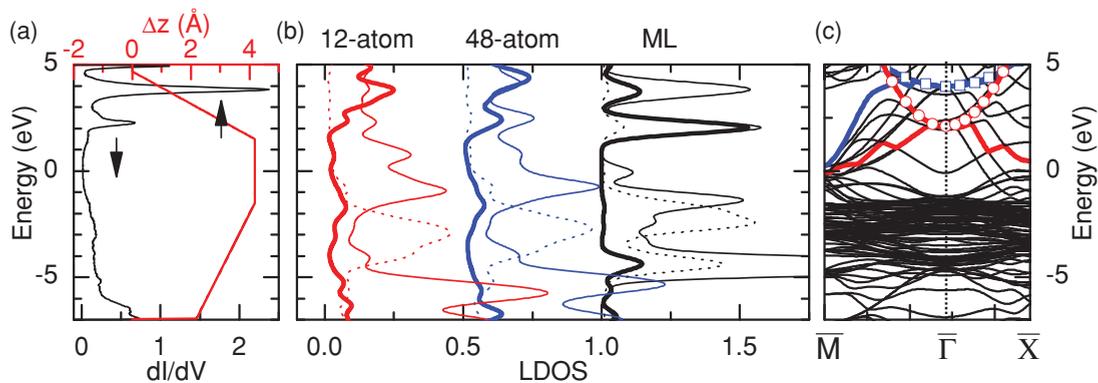


FIG. 1. (Color online) Comparison of experimental and calculated electronic structure of Cu_2N . (a) Tunneling spectroscopy of an $\sim 40 \text{ nm}^2$ island in z -ramp mode. The initial tip height was set at 5 V, 1 nA. Shown in red is the relative tip height as voltage is varied. (b) Calculated LDOS for monolayer (ML) coverage (black), and 48 atom (blue) and 12 atom (red) islands. Total LDOS is projected onto N (thin solid lines) and Cu (dotted lines, $\times 1/8$) atomic sites. Thick solid lines are the N-site s -state projection ($\times 4$ for 12,48 atom islands, $\times 2$ for ML). For clarity, LDOS for 48 atom and ML coverages are shifted by 0.5 and 1.0 units, respectively. (c) Calculated band structure for a Cu_2N monolayer. Highlighted in red and blue are the two unoccupied Cu_2N bands. Open symbols show parabolic fits near Γ .

k -points centered on Γ , but only covering a small fraction of the surface Brillouin zone. The mesh size and areal density were maintained with successively larger unit cells for consistent numerical precision. We calculated total and projected (s -, p -, d -orbital) LDOS at N and Cu sites within Cu_2N . The LDOS was convolved with a Gaussian function (full width at half max of $\sim 0.65 \text{ eV}$) to produce representative spectra, given intrinsic noise in the calculations due to the finite system size (i.e., 16, 382, and 134 atoms for ML, $\text{Cu}_{32}\text{N}_{16}$, and Cu_8N_4 islands, respectively), numerical precision, and periodic boundary conditions.²¹

Figure 1 compares measured dI/dV spectra (Fig. 1(a)) with calculated LDOS (Fig. 1(b)) and band structure (Fig. 1(c)). The data in Fig. 1(a) were acquired with the tip positioned over the center of an $\sim 40 \text{ nm}^2$ island, i.e., large enough to approximate the spectra for monolayer films.¹² Peaks at 2.2 and 3.8 V represent unoccupied states, which are the main focus of this paper. No prominent occupied states were observed at negative voltage. Rather, a gradual rise in state density starting at -1 V was followed by a sharper rise at -5.5 V . Because tunneling at large negative voltages is dominated by electrons near the sample's Fermi energy, it is difficult to probe occupied states over such a range. While the relative heights of features in Fig. 1(a) are sensitive to the exact tip trajectory, these characteristic features are reproduced in constant height and current modes.¹⁰

The calculated band structure of monolayer Cu_2N films (Fig. 1(c)) is in good agreement with our STM measurements, as well as prior DFT calculations and photoelectron spectroscopy studies.²² Unoccupied bands are observed, with groupings near $+2 \text{ eV}$ and $+4 \text{ eV}$ at the Γ point. A dense grouping of occupied states beginning at -2 eV is attributed to the onset of Cu d -states.²³ The most prominent N-derived states begin at -5 eV , similar to the onset in dI/dV in Fig. 1(a).

The set of black curves for monolayer Cu_2N in Fig. 1(b) shows the total and s -state LDOS, projected onto an N atom, as well as the total LDOS projected onto a Cu atom. Qualitatively similar features are found in the total LDOS for N and Cu sites, although the d -states are more prominent for Cu sites.

Experimental dI/dV spectra do not depend on whether the tip is positioned over a Cu or N site, suggesting spatial averaging over several sites. The peaks at positive voltage in dI/dV correspond well to unoccupied states in the LDOS at similar energies. However, some occupied states in the total LDOS (e.g., 0, -1.5 eV) do not appear as peaks in dI/dV . We find better agreement with the s -state projected LDOS. This may reflect increased overlap between s -states and the tip's atomic orbitals,^{24,25} although the atomic termination of the STM tip is not well known. We compare the size-dependent LDOS in Fig. 1(b) with experiment below.

The simple particle-in-a-box model has provided a qualitative understanding of quantum confinement in surface nanostructures such as quantum corrals,¹ adsorbate islands,^{3,4} and vacancy islands.²⁶ Electrons can be similarly confined to the Cu_2N islands.²⁷ Figure 2(a) compares dI/dV spectra taken near the 2 eV state with the tip positioned over the center or corner of the island shown in Fig. 2(b). These data indicate a series of peaks, the relative intensity of which varies with tip position. Spatial maps of dI/dV reveal standing-wave patterns for the confined electrons (Figs. 2(c)–2(f)). The energy levels of an electron in a two-dimensional square box with infinitely high walls are given by:

$$E(n_x, n_y) = \frac{\hbar^2 \pi^2}{2m^*} \left(\frac{n_x^2}{A} + \frac{n_y^2}{A} \right) + E_0. \quad (1)$$

Here, E_0 is the state energy for an infinite-size box, n_x and n_y denote the energy levels, m^* is the effective mass, and A is the area of the box. The probability densities of eigenstates $|\psi_n|^2$ can be calculated analytically (insets in Figs. 2(c)–2(f)), and they are in good qualitative agreement with the experimental images. The effective mass for the 2 eV Cu_2N state, $m^* \approx 0.7 m_e$, can be calculated from the spacing between levels (e.g., the [1,1] and [1,3/3,1] levels in Figs. 2(c) and 2(e)). For comparison, we calculated m^* of the corresponding band from our DFT band structure. Shown in red in Fig. 1(c), the band is approximately parabolic near Γ , and it can be fit with the equation: $E(k) = \frac{\hbar^2 k^2}{2m^*} + E_0$, using an effective mass of $m^* =$

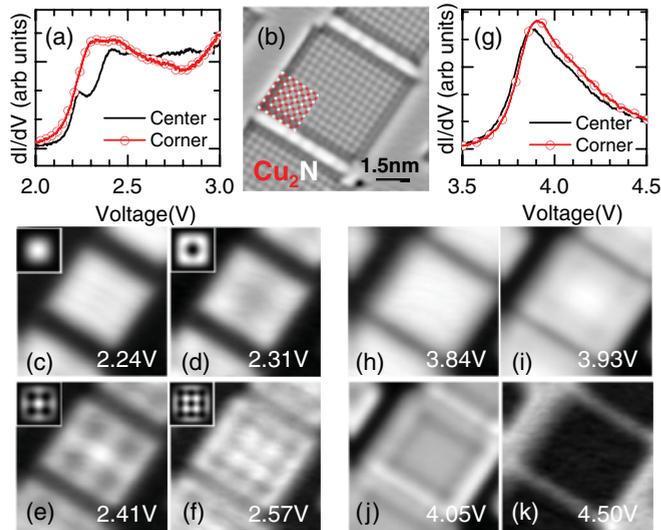


FIG. 2. (Color online) Quantum confinement in Cu_2N . (a,g) Tunneling spectroscopy with the tip positioned at the center and corner of the $\sim 29 \text{ nm}^2$ island imaged in (b). The tip height was set at 3 V, 1 nA in (a) and 5 V, 0.5 nA in (g). The STM image in (b) was Laplace filtered to enhance contrast of the atomic lattice. A schematic showing Cu and N atomic positions is overlaid on part of the image (0.5 V, 1 nA). (c)–(f) Spatial maps of dI/dV near 2 V. Insets show probability density calculated using the simple particle-in-a-box model. (h)–(k) Spatial maps of dI/dV near 4 V.

$0.85 m_e$ and $E_0 = 2.1 \text{ eV}$, which is in reasonable agreement with experimental values.

Figures 2(g)–2(d) show corresponding data near the 4 eV state. In this case, it is difficult to resolve any distinct peaks in tunneling spectroscopy, and only slight variation is observed with tip position. Spatial images of dI/dV show the ground state at $\sim 3.9 \text{ V}$, but they do not clearly show any higher excited states (Figs. 2(j) and 2(k)). To understand these differences, we consider the effective masses of the two bands. The reduced curvature of the 4 eV band in our DFT calculations (blue curve in Fig. 1(c)) indicates a larger effective mass $m^* = 2.4 m_e$. From Eq. (1), the separation and spacing of confined levels from the band edge are inversely proportional to m^* , so that a weaker confinement effect is expected for bands with larger m^* . Given the intrinsic line width of these states ($>0.1 \text{ eV}$), tunneling spectra and dI/dV images reflect the superposition of overlapping states, so that no single state can be resolved.

We studied the evolution of quantum confinement down to 0.5 nm^2 islands (corresponding to Cu_8N_4). In determining island areas from STM images (e.g., Fig. 3(a)), we considered broadening of island edges due to experimental (e.g., finite tip sharpness) and intrinsic (e.g., wave function leakage) sources.⁴ We defined the perimeter in atomic-resolution images as corresponding to one Cu layer beyond the boundary of N atoms (cf. Fig. 3(c)). For islands in our data set where atomic-resolution images were not obtained, we used a threshold technique to measure island areas.²⁸ At low voltage ($<2.8 \text{ V}$), an island appears as a 0.18 nm depression relative to the bare Cu(100) surface. We chose a threshold of 30% of this depth for determining the island perimeter; this yielded an area consistent with the geometric area determined by counting atoms in atomic-resolution images (cf. contour in Fig. 3(c)).

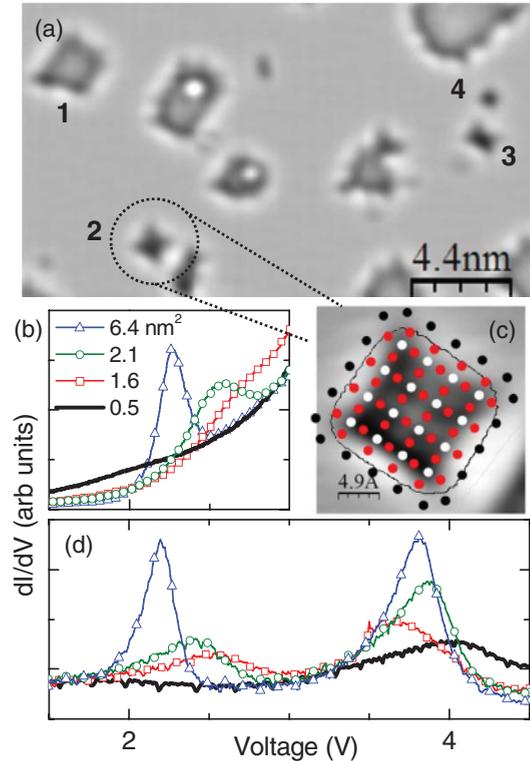


FIG. 3. (Color online) Emergence of electronic states in nanoscale Cu_2N islands. (a) STM image showing four islands: (1) irregular square, 6.4 nm^2 ; (2) square island ($\text{Cu}_{32}\text{N}_{16}$), 2.1 nm^2 ; (3) rectangular island ($\text{Cu}_{24}\text{N}_{12}$), 1.6 nm^2 ; (4) square island (Cu_8N_4), 0.5 nm^2 (0.108 V, 0.1 nA). (b) Tunneling spectroscopy (constant height mode) near the 2 eV state (3V, 1 nA). (c) High-resolution image of island #2, showing the lattice of Cu and N atoms. The contour represents the 30% threshold used to determine island area when atomic-resolution images were not available. (d) Tunneling spectroscopy (constant current mode) (0.25 nA).

We estimated the error in this method as the average variation in area for $\pm 5\%$ changes in the threshold condition.

Figure 3(b) shows that the 2 eV state shifts toward higher energy as island area decreases, until it is no longer clearly observed in the smallest islands studied. The shift is summarized in Fig. 4 for a data set of 43 islands. Here, the ground state energy was determined by fitting the lowest-energy peak of spectra taken above the center of the islands. The scatter is likely due to shape variations, because many of the islands studied were not perfectly square. As expected from Eq. (1), the ground state energy is inversely proportional to island area. The linear trend suggests that the effective electron mass is independent of island area in this range; the slope gives $m^* \approx 0.98 \pm 0.08 m_e$. The difference between this value and that obtained from the standing-wave patterns on a single island ($0.7 m_e$) likely indicates that our choice for defining the island perimeter underestimates the effective area of the island. As discussed previously,²⁹ the wave functions of confined electrons may leak beyond the island boundaries. The leakage correction lowers m^* and would be more important for the smaller islands in Fig. 4 than for the large island in Fig. 2. An effective mass $m^* = 0.85 \pm 0.1 m_e$, which is in better agreement with the standing-wave patterns and DFT calculations, is obtained using a 20% threshold criterion, i.e.,

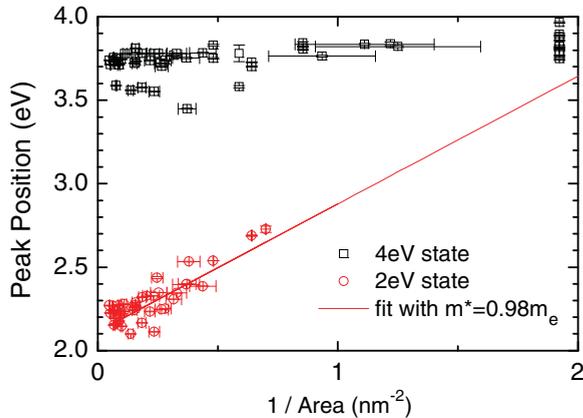


FIG. 4. (Color online) Evolution of electronic states with island area. Shown are ground state peak positions for the 2 eV state (from constant height spectroscopy), and 4 eV state (from constant current spectroscopy). The solid line is a best fit using $m^* = 0.98 m_e$.

roughly corresponding to an extra row of Cu atoms around the island perimeter.

We employed the “constant current” mode to simultaneously monitor the evolution of both states with island area (Fig. 3(d)). Figure 4 shows that in contrast to the 2 V peak, it is difficult to determine a systematic shift of the 4 V peak. This likely indicates that the smaller shift expected for the heavier mass band is less than experimental uncertainties due to shape variation or environmental contributions, such as coupling to neighboring islands or point defects. Such environmental effects may explain why the rectangular island #3 in Fig. 3 exhibits a lower voltage peak (~ 3.7 V) than expected. Variation in the STM tip’s sharpness or tip height (which differs by ~ 0.2 nm when probing the 2 eV and 4 eV states)¹⁰ can also contribute to systematic error, particularly for the smallest islands. For example, we found an ~ 0.1 V variation in peak position between sharp and blunt tips in studying several identical 0.5 nm² islands (i.e., data at $1/A = 1.9$ nm⁻² in Fig. 4). This may indicate that the surrounding Cu contributes to the spatially averaged dI/dV probed by blunt tips over small islands.

Figures 3(b) and 3(d) show that both Cu₂N states can be clearly observed in islands down to ~ 1.5 nm². The 2 eV state is not observed in smaller islands, such as the 0.5 nm² island in Fig. 3(d), which only shows a weak peak associated with the 4 eV state. Although the particle-in-a-box model provides good qualitative agreement for larger islands, it neglects aspects of the physical system that may be important for smaller islands. It is difficult, for example, to measure the finite height barrier that confines electrons to the Cu₂N islands. A lower bound is 4 eV, since we still observe the confined ground state for the 4 eV band. A reasonable upper bound is the Cu₂N work function, which we previously measured to be ~ 5.5 eV.¹⁰ In a finite height box with decreasing area, it is possible that the lower mass electrons in the ground state of the 2 eV band can

no longer be confined, while the higher mass electrons in the 4 eV band can still be confined. However, extrapolation of the linear fit in Fig. 4 to smaller islands suggests that electrons in the 2 eV band should still be confined, given our constraints on the barrier height.

We speculate that the disappearance of the 2 eV state in the smallest islands reflects a size-dependent coupling to available Cu states. At the Γ point, the projected band structure of the Cu(100) surface has an unoccupied surface state at ~ 1.8 eV and a gap from 1.8 eV to 7 eV.³⁰ Electrons in the 2 eV state of Cu₂N may leak out from islands into the Cu surface state. The larger ratio of perimeter to area in smaller islands may increase the matrix elements coupling electrons in Cu₂N to the Cu surface state. This increased coupling could be responsible for the broadening with decreasing area illustrated in Fig. 3(b). Similar broadening trends have been observed in other systems and are typically attributed to lossy scattering at the island boundaries.⁴ In contrast, the 4 eV Cu₂N state lies well within the projected band gap of the Cu(100) surface, and it is not near in energy to any Cu surface states. Leakage may still occur into bulk states, which can account for the observed broadening with decreasing area. However, the lack of available surface states may explain why the 4 eV state persists in the smallest islands studied (0.5 nm²), consisting of only 12 atoms.

This hypothesis is qualitatively consistent with our DFT calculations. Figure 1(b) shows calculated LDOS for 48 and 12 atom square islands, corresponding to islands #2 and #4, respectively, in Fig. 3(a). Given the intrinsic noise in calculated LDOS from finite size systems, the quantum-confined shifts of these states are difficult to resolve. However, we do find that the LDOS peak associated with the 2 eV state is reduced in the 48 atom island compared to the full monolayer, and it is no longer visible in the 12 atom island. The LDOS associated with the 4 eV state also decreases, but a peak can still be observed in the smallest 12 atom islands. This trend is particularly clear in the *s*-state-projected LDOS (bold curves in Fig. 1(b)). Furthermore, LDOS projected onto Cu sites within the Cu₂N islands (dashed curves) indicates that the 2 eV state has more Cu character than the 4 eV state, which may also facilitate the coupling to Cu surface states.

In summary, we demonstrate that a combination of scanning tunneling microscopy and density functional theory calculations is useful for studying the emergence of electronic states in nanoscale islands. Further extension of these methods will help in understanding the development of collective states in few-atom systems.

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