Electron Confinement to Nanoscale Ag Islands on Ag(111): A Quantitative Study

Jiutao Li* and Wolf-Dieter Schneider
Institut de Physique Expérimentale, Université de Lausanne, CH-1015 Lausanne, Switzerland

Richard Berndt
Physikalisches Institut, RWTH Aachen, D-52056 Aachen, Germany

S. Crampin
Department of Physics, University of Bath, BA2 7AY, United Kingdom
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Lateral confinement has been suggested as a possible mechanism for depopulation of surface state levels and concomitant modification of metal surface related properties. Studies to date give conflicting accounts of the effectiveness of confinement due to scattering at step edges. We present a quantitative study of surface states on nanoscale Ag islands on Ag(111), using low-temperature scanning tunneling microscopy and electronic structure calculations. These results confirm the validity of the confinement picture down to the smallest of island sizes. [S0031-9007(98)05820-7]

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There are electrons on the close-packed faces of the noble metals which occupy surface states, quasi-two-dimensional states localized at the metal surface and which have nearly free-electron-like dispersion [1]. In recent years there has been a renaissance of interest in the physics of these electrons, which it is argued play an important role in a variety of physical processes, including epitaxial growth [2], in determining equilibrium crystal shapes [3], in surface catalysis [4], in molecular ordering [5], and in atom sticking [6]. This attention may be largely attributed to the advent of the scanning tunneling microscope (STM), which has enabled direct imaging in real space of electrons in surface states, and their interactions with adsorbates [7], steps [8,9], and other structures [9,10]. Probably the most striking observation has been of the confinement of surface state electrons within artificial nanoscale structures [10], geometrical arrays of Fe atoms positioned with atomic scale precision using the STM, and which have also received theoretical attention [11–14]. Scattering at natural structures such as steps has also been seen to result in lateral localization [9].

Confinement is important as it raises the energies of the surface state electrons, resulting in a depopulation of the surface state band and a concomitant modification of surface properties associated with the surface state electrons [2–4]. However, to date there has been little attention paid to the systematics of the confinement, especially in the limit of smaller scale structures. Can one still talk of surface state electrons supported on a structure just three or four atoms wide? These structures are the ones most likely to result in significant depopulation, and exist naturally on surfaces especially during epitaxial growth. In contrast to the corral studies of Ref. [10], a recent angle-resolved photoemission study [15] on vicinal Cu(111) surfaces with monatomic steps spaced ~ 1.5 nm apart has found shifts in surface state energies only a fraction of those expected on the basis of ideal confinement, suggesting the step edges act only as weak and permeable barriers. Thus, the validity of confinement as a mechanism of surface state depopulation is in question.

In this Letter we report a study of surface state electrons confined to small Ag islands on Ag(111) [16]. In contrast to adatom corrals, these are stable structures even at elevated bias voltages in the STM, enabling us to observe standing waves over a wide range of voltages. Complementary electronic structure calculations enable us to extend the investigation down to the smallest island sizes, quantifying the nature of surface state confinement.

Our experiments are performed in a custom-built ultrahigh vacuum (UHV) STM [17] operating at temperatures of $T = 5$, 50, and 295 K. We use electrochemically etched W tips prepared in UHV by heating and Ar^+ bombardment. A Ag(111) substrate, cleaned by sputter-anneal cycles in UHV, is exposed to Ar^+ bombardment in order to create nucleation sites. Subsequent Ag deposition at room temperature leads to the formation of Ag adatom islands of monatomic height. Once a suitable distribution of island sizes has been prepared, the sample is cooled in order to freeze the island structure. In Fig. 1 we present a typical image following this procedure, showing the coexistence of monolayer-high adatom islands and a number of smaller but more numerous vacancy islands (due to the ion bombardment). The crystalline symmetry leads both to adopt approximately hexagonal shapes. In our STM studies, we acquire simultaneously spectroscopic (differential conductance, dI/dV) and constant current images ($V_{\mathrm{rms}} = 2$–4 mV modulation at ~ 23 kHz added to the bias). Local spectroscopy of dI/dV versus the sample voltage V is performed under open feedback loop conditions (modulation at ~ 230 Hz).

Differential conductance maps taken above individual islands exhibit strongly voltage-dependent features.

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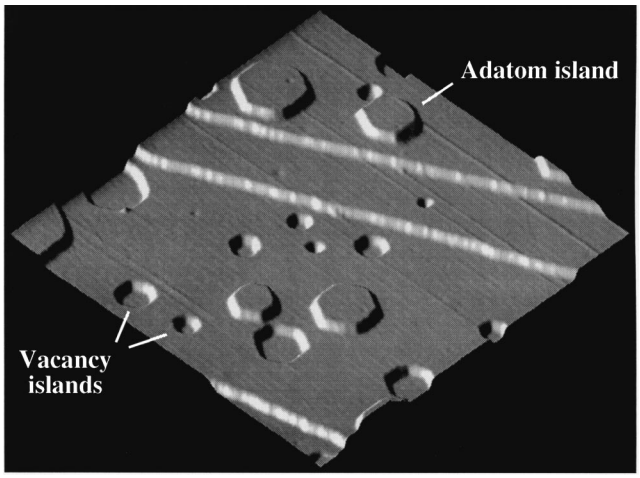

FIG. 1. STM constant current topograph of Ag adatom islands and vacancy islands on Ag(111) taken at $T = 50$ K, $V = 400$ mV and $I = 1$ nA, size approximately 160×160 nm^2. Also present are several monatomic steps.

Figure 2 shows a typical series of scans taken above an island. For voltages around -65 mV and lower (negative voltage corresponds to tunneling from the sample) the image of the interior of the island is featureless. At higher voltages we observe standing wave patterns of increasing complexity, beginning with a single peak near the center of the island and gradually evolving to multiple rings with sixfold azimuthal modulations, which are partially distorted by deviations of the island shape from hexagonal symmetry. STM measurements of dI/dV are related to the local density of states (LDOS) above the surface [18], and the standing waves may be identified as originating from surface state electrons, confined by the rapidly rising potential at the edges of the island. On the clean surface the surface state disperses upwards from $E_0 = -67$ meV, with an effective mass $m^* = 0.42$ [19,20].

Positioning the STM tip above the center of a particular island and recording dI/dV spectra, we observe a series of peaks. Figure 3(a) shows a typical spectrum, which is reminiscent of those measured at the center of adatom corrals [10]. The peaks correspond to energy levels of the confined surface state electrons broadened into resonances by single-particle scattering processes [11,12], many-body interactions [13], and instrumental effects such as thermal broadening. To complement these experimental measurements we have performed electronic structure calculations on small Ag islands on Ag(111), using the multiple-scattering approach described in Refs. [13,21]. We solve the single-particle Dyson equation $G = G_0 + G_0 \Delta V G$ to find the energy-dependent Green function $G(\mathbf{r}, \mathbf{r}'; E)$, with the Green function for the clean surface used as the reference Green function G_0 and ΔV the change in potential due to the presence of the adatom island. The LDOS at $\mathbf{r}$ is given by $n(\mathbf{r}, E) = (1/\pi)\Im G(\mathbf{r}, \mathbf{r}; E)$. Working within the atomic sphere approximation, we assume ΔV is spatially restricted to the Ag adatom sites and the neighboring sites on the vacuum side. Tests on small islands have confirmed the accuracy of this approximation. We take the potentials from *ab initio* calculations of the clean surface, which give the binding energy and effective mass of the surface state band as $E_0 = -72$ meV and $m^* = 0.37$.

We have considered regular hexagonal islands with sizes up to 631 atoms. Figure 3(b) shows the LDOS calculated 0.75 nm above the center of various Ag adatom islands, showing the resonances arising from electron confinement. As the island size decreases, the levels rise markedly, consistent with a high degree of confinement.

To quantify the nature of the confinement we analyze the energy levels in Fig. 3 in terms of two-dimensional "particle-in-a-box" eigenstates, corresponding to electrons with effective mass m^* confined within a hexagonal domain of potential E_0 by infinitely high barriers. This is not a separable problem, contrary to the situation with circular or rectangular geometry. We perform a numerical treatment using an embedding technique [22], imposing the zero-amplitude boundary conditions at the surface of the hexagon variationally.

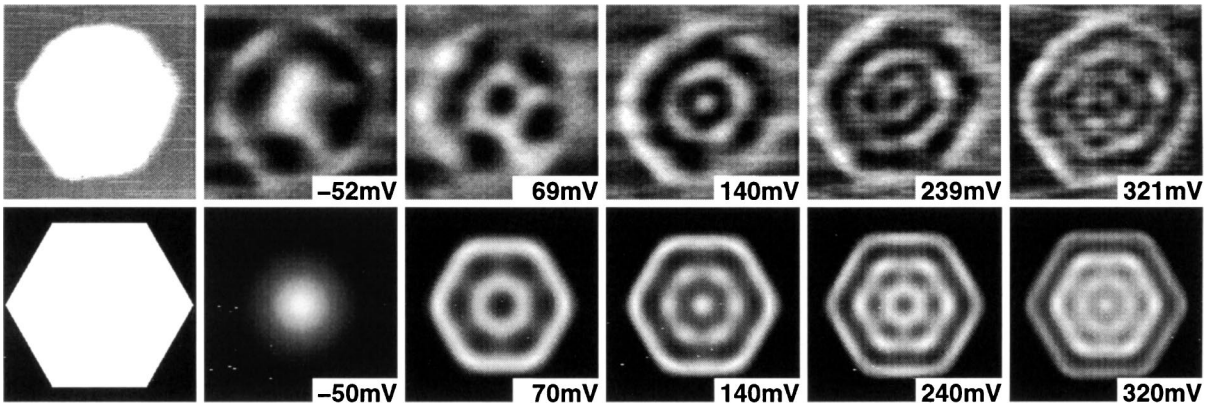

FIG. 2. Upper row: topographic image of an approximately hexagonal Ag island on Ag(111) (area ~ 94 nm^2), and a series of dI/dV maps recorded at various bias voltages (at $T = 50$ K). Lower: geometry of a hexagonal box confining a two-dimensional electron gas, and the resulting local density of states. Experimental values have been used for the surface state onset E_0, electron effective mass m^*, and the island size. The calculations include a self-energy of $\Gamma = 0.2(E - E_0)$.

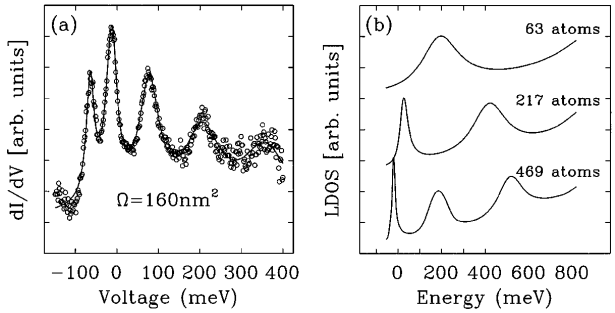

FIG. 3. (a) dI/dV spectrum taken (at $T = 50$ K) with the STM tip positioned above the center of a hexagonal Ag island on Ag(111), area $\Omega = 160$ nm^2. The line is the result of a five-Lorentzian fit to the experimental data. (b) Local density of states calculated 0.75 nm above the center of variously sized monatomic hexagonal Ag islands on Ag(111).

The eigenvalues scale with the inverse of the area of the hexagon, Ω. In atomic units ($\hbar = m_e = e^2 = 1$)

$$E_n = E_0 + \frac{\lambda_n}{m^*\Omega}, \qquad n = 1, 2, 3 \ldots . \tag{1}$$

Only eigenstates which transform according the A_1 representation of the group C_6 (6mm) of the hexagon [23] have a nonzero amplitude at the origin, and for these we find the lowest few are $\lambda_1 = 9.296$, $\lambda_4 = 48.70$, and $\lambda_{10} = 117.0$. In comparing with the experimental dI/dV data and/or the multiple-scattering calculations, we do not know *a priori* what the relevant size of an island is. In the present case the confinement is effected by the rapid rise in the potential beyond the edges of the island. However, a sizeable fraction of the surface state extends into the first few layers of atoms and so will not be directly influenced by the island edge. It is, therefore, not clear where the effective boundary confining the surface state electrons is, relative to either the measured topological line scan of the island or the actual positions of the edge atoms. To circumvent this difficulty we attempt to *fit* the results from the scattering calculations with the energies from Eq. (1), assuming the effective boundary lies a constant distance (independent of island size) beyond the positions of the edge atoms. This distance is the only fitting parameter. The scattering calculations are then used to simulate constant current topographs by evaluating the integrated LDOS above the surface, enabling us to identify *theoretically* where on a topographical cross section the effective boundary is located.

Figure 4 shows the result of this analysis. In the inset we present an STM topographical line scan recorded above a small Ag island, showing the characteristic flat plateau and broad edges. The location we identify as the effective boundary of the surface state electrons lies close to the midpoint of the rise in the topological line scan, ~0.5 nm beyond the edge atoms [24]. With this definition, we find remarkable agreement between the energies of the surface state electrons as derived from both experimental dI/dV spectra and the theoretical LDOS, compared to the scaling

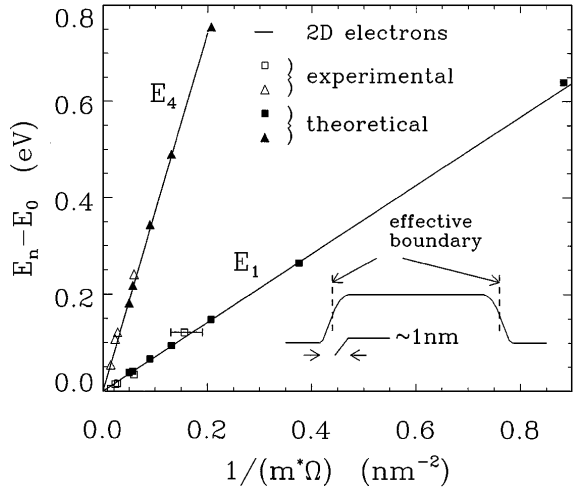

FIG. 4. Energies of the lowest two confined surface state levels at the center of variously sized hexagonal Ag islands on Ag(111) as a function of renormalized inverse area. Comparison between measured energies (open symbols; error from experimental determination of the island size is indicated when larger than symbol size [25]), energies predicted by multiple-scattering calculations (filled symbols), and the behavior expected of a perfectly confined two-dimensional electron gas (lines). Inset: measured topological cross section of a Ag island, along with the position identified as the effective boundary confining surface state electrons.

behavior expected of two-dimensional electrons. Note that the smallest island in Fig. 4 contains just 19 atoms, and the smallest measured island is $\Omega \sim 16$ nm^2 containing ~100 atoms. Our results indicate that as far as the energy levels are concerned, it *is* valid to talk of surface states confined to nanoscale islands, right down to the smallest island sizes. The confinement corresponds to an infinite barrier, and the area to which the electrons are confined corresponds to a boundary lying a fixed distance beyond the outermost atoms, independent of both energy and the island size.

There are deviations from this interpretation of the electron behavior, as witnessed by the finite width of the confined energy levels in Fig. 3. The levels should be infinitely sharp for ideal confinement. The width of each energy level stripped of instrumental contributions, ΔE_n, implies a finite lifetime for the confined electrons, $\Delta t_n \simeq \hbar/\Delta E_n$, dominated by scattering into other electron states at the island edges [11–13]. While these processes do not influence the energies of the levels, one potential consequence is that depopulation of the surface state becomes significant only for island sizes smaller than those derived from a two-dimensional analysis. Even at $T = 0$ each energy level will have a finite width, resulting in partial occupation *after* the level has risen above the Fermi energy. Assuming a Lorentzian line shape, the state will be $1/4$ full when E_n lies ΔE_n above the Fermi level. For an estimate of the significance of this effect, the experimental spectra yield

$$\Delta E_n \simeq 0.2(E_n - E_0). \tag{2}$$

Using this relation, the island area at which the lowest level is $3/4$ depopulated is 10% smaller than that which yields complete depopulation assuming perfect confinement. Hence, the influence of the finite widths is marginal. We will give a more detailed analysis of the level widths elsewhere [26], but note here that incorporating them into the two-dimensional description as a self-energy provides a good model of the confined states, as shown in Fig. 2. Allowing for the clear deviations in shape of the experimental island from the ideal hexagon assumed theoretically, which (alongside the finite resolution of the STM) results in the more rounded features, there is good agreement between the theoretical and experimental images. This is not trivial, as over ten states in total contribute to the spectrum, and the correct weighting is necessary to reproduce the development in nodal features as the energy varies. The largest differences arise at the island edges, when experimental dI/dV data are influenced by tip-height variations [20] and because theoretically we do not include the background of bulk states.

To summarize, a quantitative study of electron confinement to nanoscale Ag islands on Ag(111) using low temperature STM and electronic structure calculations confirms the validity of the particle-in-a-box model for confined surface state electrons. We find the energies conform to the expected scaling behavior down to the smallest of island sizes, and that the width of the confined levels has only a marginal effect on the surface state depopulation. Note that our results may have implications beyond the island structures we consider. For larger island sizes the island edges have the same atomic structure as low-energy steps orientated along $\langle 1\bar{1}0\rangle$ directions on the (111) surface, and so our conclusions should hold also for confinement to raised terraces and to fingerlike structures characteristic of the dendritic formations which occur in the low-temperature growth of Ag/Ag(111) [27]. In addition, we expect our conclusions to hold also for confinement on Cu(111) and Au(111) surfaces, due to the similarities in the band structures of the noble metals. We believe the failure to observe these effects in angle-resolved photoemission [15] most likely results from the presence of a sizeable distribution of terrace widths within the spot area of the incident radiation.

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*Present address: Dept. of Electrical and Computer Engineering, Univ. of Illinois at Urbana-Champaign, 3025 Beckman Institute, Urbana, IL 61801.

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