Phonon Contribution to the Lifetime of Surface State Quasiparticles Confined in Nanopyramids

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(Received 7 August 2009; published 5 January 2010)

We present a scanning tunneling microscopy investigation of the dynamics of hot electrons and holes in Ag pyramidal nanostructures. The geometry of the nanostructure leads to a strong reduction of the decay mechanism into the bulk states and then to a large reflection coefficient of the surface electronic waves. Therefore, in contrast to quantum corrals and adatom islands which show a dominant lossy scattering contribution to the linewidth, the narrow observed structures in the differential conductivity spectra reveal the expected linewidth minimum at the Fermi energy. The electron-phonon contribution to the lifetime is shown to be dominant, in agreement with previous photoemission measurements.

DOI: 10.1103/PhysRevLett.104.016802 PACS numbers: 73.20.At, 61.46.Hk, 68.37.Ef, 72.10.Di

In ordinary metals, the electron excitations close to the ground state can be described by the quasiparticle concept in the framework of the Fermi liquid model [1]. The lifetime of these quasiparticle excitations is an important quantity because it characterizes the coherence length which has a fundamental role in the electronic properties like transport. A finite quasiparticle lifetime results from fundamental interactions (electron-electron and electron-phonon inelastic scattering) but also from scattering by defects and impurities. In the last decade, the dynamics of hot electrons and holes has attracted considerable attention. Techniques like scanning tunneling microscopy (STM) and spectroscopy (STS), photoemission, and two-photon photoemission have been used in order to determine spectral linewidth and lifetime of surface states [2,3]. Two different approaches using STM and STS have been developed. The first one exploits the damping of the quantum interference patterns due to the scattering of the surface state by a step edge or a quantum corral [4,5]. This method allows the determination of the lifetime up to several eV, but the low energy excitations ($E < 0.5$ eV) are excluded from the analysis because the energy dependence of the transmission factor is discarded [4]. The second one uses the linewidth of differential conductivity spectra (dI/dV) at a fixed point above the surface. Such a spectrum for the Shockley state of (111) noble metals exhibits a steplike shape, and the lifetime can be determined from the onset of the surface band [6]. More interesting to investigate the energy dependence of the lifetime is the study of the spectral linewidth of confined states in natural (adatom or vacancy islands) or artificial (quantum corrals obtained from atomic manipulation) nanostructures [7–9].

Unfortunately in these nanostructures, an additional contribution to the linewidth arises due to lossy boundary scattering. This latter mechanism, which is usually the dominating one, prevents us from directly determining the intrinsic linewidth. In order to obtain this quantity, it is then necessary to precisely model the important contribution due to the imperfect reflection of the surface state at the nanostructure boundary. Recently, a scattering model for a circular resonator of diameter L has been developed [10]. The scattering properties of the confining wall are characterized by a reflection coefficient R [11]. The width of the nth confined state with energy E_n (defined from the bottom of the surface band) in this model is

$$\Gamma_R(E_n) = -\frac{2\hbar^2}{m^*}\sqrt{\frac{2m^*E_n}{\hbar^2}}\frac{\ln|R(E_n)|}{L}, \qquad (1)$$

where m^* is the effective mass of the electron. This equation shows that for a fully reflective wall corresponding to $R = -1$ (hard-wall limit), $\Gamma_R(E_n) = 0$. Unfortunately, systematic calculations of the interaction of surface states with one-dimensional scatterers lead to the conclusion that the reflectivity is relatively weak since most cases yield around 0.3–0.4 for the reflection probability [12]. The physical meaning is simple to understand: in addition to the reflection inside of the resonator, the electronic wave can be transmitted into the neighboring surface state or even scattered towards bulk states. This prediction suggests that the total confinement of surface states within any nanostructure may not be feasible. This result was confirmed by recent measurements [9], which show that for small real resonators like quantum corrals, adatoms, or vacancy islands, the contribution due to poor reflection is much larger than the intrinsic contribution so that it is very delicate to extract the latter with accuracy. On the other hand, for large resonators, the extrinsic linewidth decreases with increasing the resonator diameter (L^{-1} dependence) but the energy separation between the confined states decreases more rapidly (as L^{-2}) so that the different resonances are no longer resolved [10,13]. Only a few spectral lines are found close to E_F preventing us from observing the minimum linewidth expected in Fermi liquid from electron-electron and electron-phonon interactions. The situation would be significantly improved for a larger reflection coefficient of the electronic wave. In order to study in detail the lifetime of low energy excitations, it is also necessary to observe many states in the vicinity to E_F.

In this Letter, we report low temperature STS measurements in truncated hexagonal Ag pyramids supported by an Ag thin film grown on a Cu(111) surface. For the first time, we observe unambiguously narrower spectral structures in the vicinity of the Fermi energy, as expected from the Fermi liquid theory. This is likely due to the peculiar geometry of the nanopyramids, which may strongly decouple the confined surface states from the neighboring surface states but also from bulk states. Then $|R|$ may be much larger than in the case of a simple adatom island, leading to a lossy scattering linewidth that is small compared to the intrinsic one. Finally, the latter is extracted and it is shown that the dominant decay mechanism close to the Fermi energy is the electron-phonon coupling.

The measurements were carried out in a UHV setup composed of a molecular beam epitaxy chamber for the elaboration and characterization of the surfaces, a scanning tunneling microscopy (STM) chamber equipped with a 5 K-Omicron STM, and a photoemission chamber with a high resolution Scienta SES 200 analyzer [14]. The dI/dV maps (and spectra) were recorded at 5 K in the open feedback loop mode using the lock-in technique with a bias modulation of 3 meV rms at 700 Hz. As the experimental spectra exhibit a 10 meV-defect contribution, the overall instrumental resolution (about 3.5 meV) leads to a negligible extra broadening less than 1 meV for the narrowest spectral feature. The Cu(111) single crystal was cleaned by several cycles of Ar$^+$ etching and annealing at 500 °C, and it was characterized by STM and Auger electron spectroscopy (AES) [15]. Ag adatoms were evaporated from a Knudsen cell at the rate of 1 ML/ min.

Deposition of 20 ML Ag on a Cu(111) single crystal at 150 K leads to the formation of Ag truncated pyramids on relatively thick (about 10–15 ML) Ag film. Similar (111) facets of gold clusters have been observed on graphite [16]. The pyramid distribution in size and height is quite large, and most of them have a hexagonal symmetry. In Fig. 1, we present STM images of two truncated nanopyramids. Both presented nanostructures consist of a stacking of four hexagonal planes with decreasing size. The corner-corner distance of the top face is, respectively, 17 nm and 25 nm. In the lower part of this figure, we plot dI/dV maps as a function of energy (vertical axis) and position (horizontal axis) along a high symmetry direction of the hexagonal face (solid lines shown in the STM images). The hot spots in this spectroscopic map correspond to the lateral localization of the confined modes of the Shockley surface state. The ground state of the confined Shockley state ($E_1 = -47$ meV and $E_1 = -41$ meV for the 25 nm and 17 nm pyramids, respectively) is characterized by a broad feature centered in the pyramid. At higher energy, the excited modes exhibit an increasing number of nodes. The localization along the line depends on the symmetry of the different states. As clearly shown on the spectroscopic maps, many states have a node in the center of the pyramid. As a consequence, all levels do not contribute to the spectrum recorded in the center of the hexagon. Finally, the bright spot associated with the resonance close to E_F is a qualitative information of the narrowness of this spectral feature.

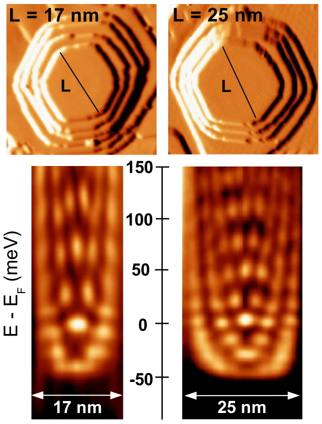

FIG. 1 (color online). Topographic STM image of a truncated hexagonal Ag pyramid and spectroscopic map obtained from 64 dI/dV spectra recorded along the line of the topographic images. It evidences the localization of the confined states in the hexagonal surface.

We report in Fig. 2 experimental dI/dV spectra recorded in two different points (A and B in the STM image). From a symmetry point of view, the different energy states exhibit the symmetry of the irreducible representation of the C_{6v} group (symmetry group of the hexagonal pyramid). Only the totally symmetric representation (usually called A_1) can exhibit a finite intensity in the central point. As examples of an A_1 symmetry, we present spectroscopic images (labeled 1 and 3) which exhibit spectral weight at the center. By moving the tip position from the A point to

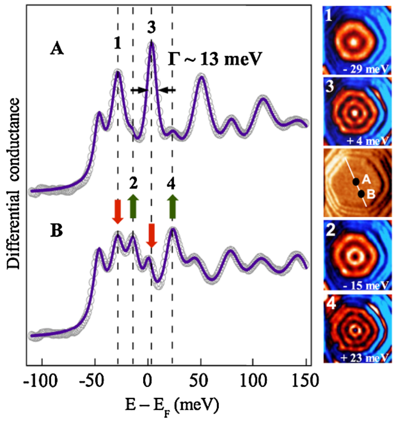

FIG. 2 (color online). dI/dV spectra recorded in the A and B points in the topographic STM image reported in the right part. The solid black line represents the fitting curve composed of Lorentzian structures associated with the confined states. In the right part, dI/dV maps are shown corresponding to the 1–4 energy, as well as a STM image showing the position of the A and B points.

the *B* point, some spectral structures (for example, 2 and 4) appear corresponding to other irreducible representations of the C_{6v} group whereas the spectral weight of the A_1 symmetry feature decreases.

Therefore, by measuring at different positions on the surface, it is possible to probe all confined surface states on the pyramid. The spectra recorded at different positions are fit by Lorentzians (solids lines in Fig. 2). The positions of these peaks determine the confined state energies (they are the same in all spectra) whereas their widths represent the total linewidth. This method allows us to determine the energy of the first 15 levels and, in contrast to many measurements in the literature which focus on spectra in the nanostructure center, we were able to study in detail the vicinity of the Fermi energy. A very good agreement is found with calculated values obtained in the framework of a two-dimensional hexagonal infinite potential quantum well. From such an analysis, it was possible to determine the zero kinetic energy (i.e., the bottom of the Shockley band in such truncated pyramids) which was found at $E = -50$ meV for both pyramids, a value which is slightly higher than the corresponding Shockley energy for the Ag(111) single crystal.

As discussed above, the spectral linewidth reflects not only the lifetime of hot electron or hole but also the contribution due to lossy boundary scattering. The intrinsic linewidth is composed of several contributions due to electron-electron ($\Gamma_{e\text{-}e}$), electron-phonon interactions ($\Gamma_{e\text{-ph}}$) and interactions with defects (Γ_{def}). Close to E_F, the Γ_{def} is energy independent, and $\Gamma_{e\text{-}e}$ is mainly quadratic [$\Gamma_{e\text{-}e} = \beta(E - E_F)^2$] but weak so that the dominant contribution is the $\Gamma_{e\text{-ph}}$. The simple Debye phonon model [17] is given by

$$\Gamma_{e\text{-ph}} = 2\pi \int \alpha^2 F(\omega) \times [1 + 2n(\omega) + f(E + \omega) - f(E - \omega)] d\omega, \quad (2)$$

where $n(\omega)$ and $f(\omega)$ are, respectively, the Bose-Einstein and the Fermi functions. $\alpha^2 F(\omega)$, the Eliasberg coupling function, is equal in a 2D system characterized by the Debye frequency ω_D to $\lambda(\omega/\omega_D)^2$. The energy dependence of the electron-phonon linewidth at low temperature ($kT \ll \omega_D$) is characterized by a pronounced increase close to ω_D and, at higher energy, a plateau which depends on the value of the electron-phonon coupling (λ) [18]. This is illustrated by the dotted line in Fig. 3 with $\lambda = 0.12$, $\omega_D = 25$ meV, and $T = 5$ K which lead to a linewidth slightly higher than obtained on a flat Ag(111) surface from photoemission [19].

Next, we have to deal with the lossy scattering contribution Γ_R. According to Eq. (1), we used the values from the literature and our own data: effective mass $m^* = 0.4m$ [8], the onset of the surface band (-50 meV). The remaining fundamental parameter is the reflection coefficient at the boundary. The energy dependence of this coefficient has been extracted from the damping of the quantum interference patterns at a step edge of the Ag(111) surface by Bürgi *et al.* [4]. This energy dependent step reflection coefficient (step coefficient in the following) was used to model the reflection extrinsic contribution in Ag islands on Ag [10,13]. In order to estimate the reflection contribution in such nanopyramids, we have first neglected the electron-electron interaction broadening (very small in this energy range) and calculated in Fig. 3 the spectral linewidth contributions due to the scattering mechanism with the step coefficient for a 17 nm pyramid. Comparison with the experimental linewidth clearly shows that the scattering properties usually observed in Ag resonators cannot describe the spectral behavior of these nanopyramids. This result strongly suggests that the reflection coefficient $|R|$ is larger than the step coefficient. Then we have calculated the linewidth with the reflection coefficient proposed for a quasi-ideal resonator [4,12] (the $|R|$ coefficient, close to 1 at the bottom of the Shockley band, remains larger than 0.75 in the investigated energy range). In both cases, we have shifted the calculated spectra by about 12 meV for a better agreement with experiments. We interpret this shift by the defect contribution. A similar defect contribution (26 meV) has been evidenced in the photoemission study of Mo(110) surface state [18]. Our analysis shows that the reflection coefficient is much larger than usually observed in nanostructures. This suggests that the scattering from the surface state to the bulk states, which corresponds to a decay of the confined states, is likely strongly reduced for this pyramidal symmetry. Step edges are far from ideal reflectors for electrons because leakage occurs into the surface state on the other side and into the bulk state of the crystal [4,12]. The situation encountered in nanopyramids seems very different. First, the transmission into the surface state of the underlying layer should probably be weak because of the height of the pyramids (4–5 atomic height).

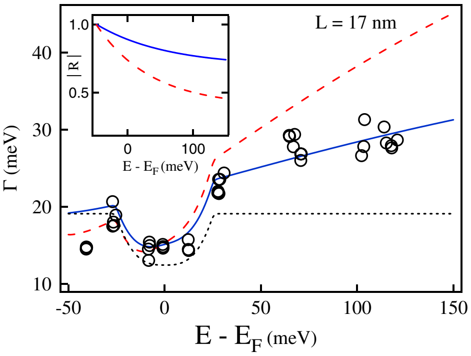

FIG. 3 (color online). Experimental spectral width of the confined states of a 17 nm pyramid (symbols). The dotted black line shows the electron-phonon scattering contribution calculated in a simple Debye model with $\omega_D = 25$ meV, $\lambda = 0.12$, and $T = 5$ K. The dashed (red) and solid (blue) lines represent the sum of the contribution of the electron-phonon interaction and lossy boundary contributions calculated with the step and quasi-ideal coefficients, respectively. These three curves have been shifted by the defect contribution (12 meV). Inset: quasi-ideal resonator (solid blue line) and step (dashed red line) reflection coefficients.

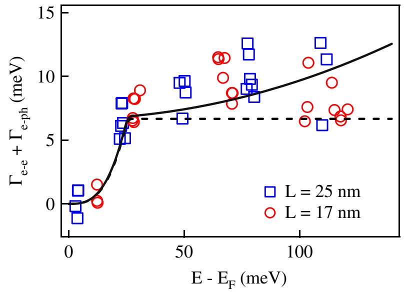

FIG. 4 (color online). Intrinsic linewidth as a function of energy for the confined states. Circles and squares correspond to the value for two different pyramid sizes $L = 17$ nm and $L = 25$ nm. The dotted line represents the electron-phonon contribution; the solid line represents the sum with the electron-electron contribution. The defect contributions are 10.7 meV and 8.5 meV for the 17 nm and 25 nm pyramids, respectively.

Second, this particular shape should also reduce the overlapping of the surface state with the bulk state leading to a reduction of the decay mechanism of the surface state into the bulk. As a consequence, $|R|$ increases leading to a decrease in the lossy boundary scattering.

In Fig. 4, we report the intrinsic part of the linewidth for two pyramids with different sizes (17 and 25 nm). The size-dependent reflection and defect contributions have been removed from the experimental spectral width. The same dependence for the different pyramids is observed confirming the validity for our analysis of the lossy boundary scattering (high $|R|$ coefficient). By exploiting the different symmetry modes, we obtain many experimental points close to E_F which allow us to precisely determine the energy dependence of the spectral width of hot electrons with small energy. This result appears for the first time in STS and confirms the photoemission measurements [19] that intrinsic linewidth is dominated by electron-phonon interaction. A small electron-electron broadening, essentially associated with the intraband decay mechanism [20,21], has been adjusted by a quadratic function with $\beta = 3 \times 10^{-4}$ meV^{-1}, in qualitative agreement with previous photoemission data [19]. However, the scattered data prevent an accurate determination of $\Gamma_{e\text{-}e}$, which requires measurement at higher energies where the $\Gamma_{e\text{-}e}$ is the dominant contribution.

In conclusion, we have performed 5 K-STS measurements on truncated silver nanopyramids. In comparison with previous studies on quantum corrals, adatoms, and vacancy islands, we have evidenced a higher reflection coefficient, i.e., a more efficient confinement of the Shockley state. This is likely due to the peculiar geometry of these nanopyramids, which reduces transmission and absorption processes. Further investigations on similar systems would be very interesting from a fundamental point of view, because it would provide a near direct access to many-body lifetimes. In the present case, we have extracted the electron-phonon lifetime, but one can imagine probing electronic interactions with other collective excitations, namely, magnons in magnetic nanopyramids. Finally, the possibility to confine the surface state more efficiently into nanostructures opens interesting perspectives for surface state engineering.

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[1] D. Pines and Ph. Nozières, *The Theory of Quantum Liquids* (Benjamin, New York, 1969).
[2] P. M. Echenique, R. Berndt, E. V. Chulkov, Th. Fauster, A. Goldman, and U. Höfer, Surf. Sci. Rep. **52**, 219 (2004) and references therein.
[3] R. Matzdorf, Surf. Sci. Rep. **30**, 153 (1998); Chem. Phys. **251**, 151 (2000).
[4] L. Bürgi, O. Jeandupeux, H. Brune, and K. Kern, Phys. Rev. Lett. **82**, 4516 (1999).
[5] K.-F. Braun and K.-H. Rieder, Phys. Rev. Lett. **88**, 096801 (2002).
[6] J. Li, W. D. Schneider, R. Berndt, O. R. Bryant, and S. Crampin, Phys. Rev. Lett. **81**, 4464 (1998).
[7] J. Li, W. D. Schneider, R. Berndt, and S. Crampin, Phys. Rev. Lett. **80**, 3332 (1998).
[8] J. Kliewer, R. Berndt, and S. Crampin, New J. Phys. **3**, 22 (2001).
[9] H. Jensen, J. Kröger, R. Berndt, and S. Crampin, Phys. Rev. B **71**, 155417 (2005).
[10] S. Crampin, H. Jensen, J. Kröger, L. Limot, and R. Berndt, Phys. Rev. B **72**, 035443 (2005).
[11] L. Bürgi, O. Jeandupeux, A. Hirstein, H. Brune, and K. Kern, Phys. Rev. Lett. **81**, 5370 (1998).
[12] G. Hörmandinger and J. B. Pendry, Phys. Rev. B **50**, 18 607 (1994).
[13] J. Kröger, L. Limot, H. Jansen, R. Berndt, S. Crampin, and E. Pehlke, Prog. Surf. Sci. **80**, 26 (2005).
[14] H. Cercellier, C. Didiot, Y. Fagot-Revurat, B. Kierren, L. Moreau, D. Malterre, and F. Reinert, Phys. Rev. B **73**, 195413 (2006).
[15] A. Bendounan, H. Cercellier, Y. Fagot-Revurat, B. Kierren, V. Yu. Yurov, and D. Malterre, Phys. Rev. B **67**, 165412 (2003).
[16] I. Barke and H. Hövel, Phys. Rev. Lett. **90**, 166801 (2003).
[17] G. Grimvall, in *The Electron-Phonon Interaction in Metals, Selected Topics in Solid State Physics*, edited by E. Wohlfarth (North-Holland, New York, 1981).
[18] T. Valla, A. V. Fedorov, P. D. Johnson, and S. L. Hulbert, Phys. Rev. Lett. **83**, 2085 (1999).
[19] A. Eiguren, B. Heilling, F. Reinert, G. Nicolay, E. V. Chulkov, V. M. Silkin, S. Hüfner, and P. M. Echenique, Phys. Rev. Lett. **88**, 066805 (2002).
[20] L. Vitali, P. Wahl, M. A. Schneider, K. Kern, V. M. Silkin, E. V. Shulkov, and P. M. Echenique, Surf. Sci. **523**, L47 (2003).
[21] M. Becker, S. Crampin, and Berndt, Appl. Phys. A **88**, 555 (2007).