Probing Hot-Electron Dynamics at Surfaces with a Cold Scanning Tunneling Microscope

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We report on a novel approach to measure the phase relaxation length and femtosecond lifetime of hot quasiparticles on metal surfaces. A 4 K scanning tunneling microscope has been used to study the spatial decay of interference patterns in the local density of states for surface state electrons on Ag(111) and Cu(111). This decay is governed by inelastic electron-electron scattering. We find a $(E - E_F)^{-2}$ energy dependence of the lifetimes for both Ag and Cu, and our values are comparable to the corresponding bulk electron lifetimes. This indicates that electron-electron interaction of hot surface state electrons with the Fermi sea is dominated by the underlying bulk electrons. [S0031-9007(99)09260-1]

The phase relaxation length L_ϕ, i.e., the distance a quasiparticle can propagate without losing its phase memory, is a key quantity in solid state physics. Quantum mechanical interference phenomena can prevail only if L_ϕ is larger than any other relevant length scale [1]. Examples include Aharonov–Bohm oscillations, quantum Hall effect, Friedel oscillations, and localization. With respect to surface physics, L_ϕ—or equivalently the lifetime τ_ϕ of the quasiparticle—is of particular interest, since it governs the dynamics of charge transfer and electronic excitations in surface chemistry [2].

Elegant experiments have been performed to determine L_ϕ of hot ballistic electrons in low-density high-mobility two-dimensional electron gases (2DEG) present at the interfaces of semiconductor heterostructures. In particular, the excess energy and temperature dependence of L_ϕ in GaAs/AlGaAs heterostructures has been measured by Yacoby *et al.* [3] and Murphy *et al.* [4], respectively, where the main contribution to their L_ϕ could be attributed to electron-electron (*e-e*) scattering, in striking agreement with Fermi liquid theory (FLT) for a 2DEG [5,6]. Another access to electron and hole lifetimes (and hence to L_ϕ) has become possible through electron spectroscopic methods on single-crystal metal surfaces [7]. In particular, photohole lifetimes of noble metal surface states have been investigated with high-resolution angle-resolved photoemission (ARP) [8–10]. Although the phonon contribution to copper surface state lifetimes has been successfully determined with ARP [10], the assignment of ARP linewidths to true quasiparticle lifetimes is complicated by nonlifetime effects [11], and hence the absolute values of ARP lifetimes have to be considered as lower limits [10]. Furthermore, recent femtosecond time-resolved two-photon photoemission (2PPE) experiments opened up a new path to measure excess energy dependent lifetimes of hot bulk quasiparticles for metals and semimetals [12–16]. But due to cascade and depopulation effects the interpretation of 2PPE spectra is a difficult task, and up to now it does not seem to be clear why dif-

ferent groups report lifetimes which vary by up to a factor of 4 for the very same system [14,16].

Recently STM has been used to determine the lifetime of excited holes at the band edge of the Ag(111) surface state by Li *et al.* [17]. Similar to ARP Li *et al.* have investigated the linewidth of the surface state onset in tunneling spectra. The advantage over ARP is the capability to choose a surface spot bare of impurities, and hence nonlifetime effects are reduced. But with the method used by Li *et al.*, L_ϕ of excited holes at only one energy (at $\overline{\Gamma}$) can be studied, which constitutes a major limitation.

In this Letter, we present a new approach to measure lifetimes of hot surface state and surface resonance electrons as a function of excess energy locally with a 4 K scanning tunneling microscope (STM). (The term surface states shall include surface resonances for the following.) To do so we have studied the decay of quantum mechanical interference patterns from surface state electrons scattering off descending straight step edges, which of course is influenced by the loss of coherence and hence by L_ϕ. Through the dI/dV modus STM offers the possibility to map spatial variations in the local density of states (LDOS) [18,19], and with a simple model we have been able to extract $L_\phi(E)$ and thus $\tau_\phi(E)$ from such dI/dV scans at step edges for the Shockley type surface states on Ag(111) and Cu(111).

The experiments were performed with a homebuilt low-temperature UHV STM described elsewhere [20]. The Ag(111) and Cu(111) surfaces have been cleaned by sputter-anneal cycles. They showed terraces of several 1000 Å width with less than 0.05% impurity atoms of unknown chemical identity. All measurements have been performed at $T = 4.9$ K, with a tungsten tip and the bias voltage V applied to the sample. The dI/dV images have been acquired by lock-in technique with a sinusoidal bias modulation by ΔV (peak to peak). With $\sim$5.5 kHz the frequency of the bias modulation has been chosen above the bandwidth of the feedback loop.

Figure 1 shows a constant current image of a Cu(111) step edge at $V = 1.4$ V in (a) and the dI/dV image taken simultaneously in (b). Since dI/dV is a quantity roughly proportional to the surface LDOS [21] the clearly visible spatial oscillations in Fig. 1(b) are a direct consequence of Friedel oscillations in the LDOS of the 2D surface state electron gas which are induced by every static scattering center (e.g., step edges and point defects). For our experiment we have chosen straight step edges with a defect free area larger than $250 \text{ Å} \times 250 \text{ Å}$ on the adjacent upper terrace (Fig. 1). By doing so we are sure that the local elastic mean free path L_m is considerably larger than the measured L_ϕ [1], and thus the LDOS oscillations at the step are not influenced by other static scattering centers. In order to evaluate the decay of the standing waves away from straight step edges as shown in Fig. 1 the dI/dV images have been slightly rotated to align the step edge vertically, and then we have averaged the dI/dV data over several line scans. Typical averaged dI/dV data are presented in Fig. 2(a).

To interpret our data we use elastic tunneling theory, i.e., the tunneling current I is given by

$$I(V,T,x,z) \propto \int_{-\infty}^{\infty} \mathcal{T}(E,V,z)\rho_s(E,x)\rho_t(E - eV)$$
$$\times \left[f(E - eV,T) - f(E,T)\right]dE, \quad (1)$$

where T is the temperature, x characterizes the lateral position, z is the distance between surface and tip, ρ_s is the surface LDOS, and $f(E,T)$ is the Fermi function. The tip LDOS ρ_t is assumed to be a constant since we are interested only in lateral variations of dI/dV. The transmission factor $\mathcal{T}$ is given by $\mathcal{T}(E,V,z) =$

$e^{-z\sqrt{2m_e/\hbar^2}(\sqrt{W_t - E + eV} + \sqrt{-E(1-m^*/m_e) - m^*/m_e E_0^{2D} + W_s})}$, where m^* and E_0^{2D} are the effective mass and the band edge of the surface state, respectively, and W_t is the work function of the tip [21]. (Energies are given with respect to the Fermi energy.) The work function of the sample, W_s, can be considered constant for our purposes since we have found its reduction at steps due to the Smoluchowski effect to be localized to ± 3 Å around the step edge. As shown by ARP [8–10] and STM [18,19] the Shockley type surface states on noble metals form a quasifree 2D electron gas. Thus, in the presence of a straight step edge extending infinitely in y direction, ρ_s is readily calculated to yield

$$\rho_s(E,x) = \rho_b + \frac{2L_0}{\pi}\int_0^{k_E} dq$$
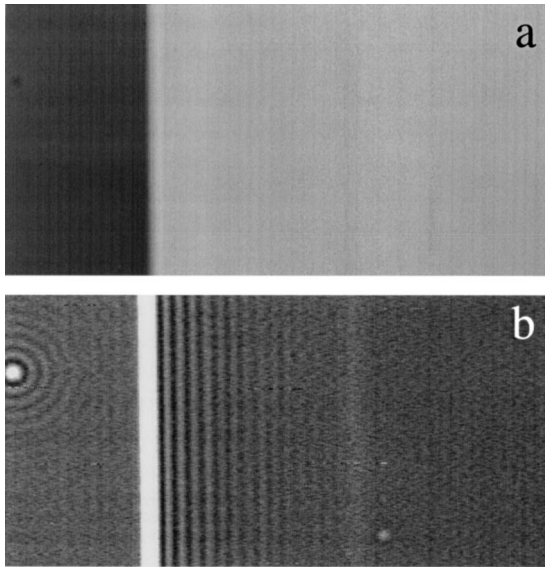$$\times \frac{1 - r(q)e^{-2(xk_E/qL_\phi)}\cos(2qx)}{\sqrt{k_E^2 - q^2}}, \quad (2)$$

FIG. 2. (a) Typical dI/dV data perpendicular to a descending Cu(111) step obtained by averaging over several line scans of a dI/dV image as shown in Fig. 1(b). The data at 1 and 2 eV were taken with a stabilizing current of 5 and 10 nA and a ΔV of 119 and 156 mV, respectively. The solid lines depict the fits with Eqs. (4) and (5). The significance of the deduced L_ϕ is demonstrated by the dashed line: neglecting inelastic processes by setting $L_\phi = \infty$ leads to a much slower decay rate than observed. (b) Comparison between the full calculation of dI/dV with Eqs. (1) and (3) and the result obtained by setting $\mathcal{T}$ constant ($T \to 0$, $L_\phi \to \infty$, typical Cu(111) parameters: $W_s = W_t = 4.5$ eV, $r = 0.5$ [23]).

FIG. 1. (a) Constant current image of a Cu(111) step edge: $280 \text{ Å} \times 138 \text{ Å}$, $V = 1.4$ V, $I = 7$ nA. (b) dI/dV image taken simultaneously with (a) by lock-in technique ($\Delta V = 135$ mV). Standing wave patterns at static scatterers as steps and impurities are clearly visible.
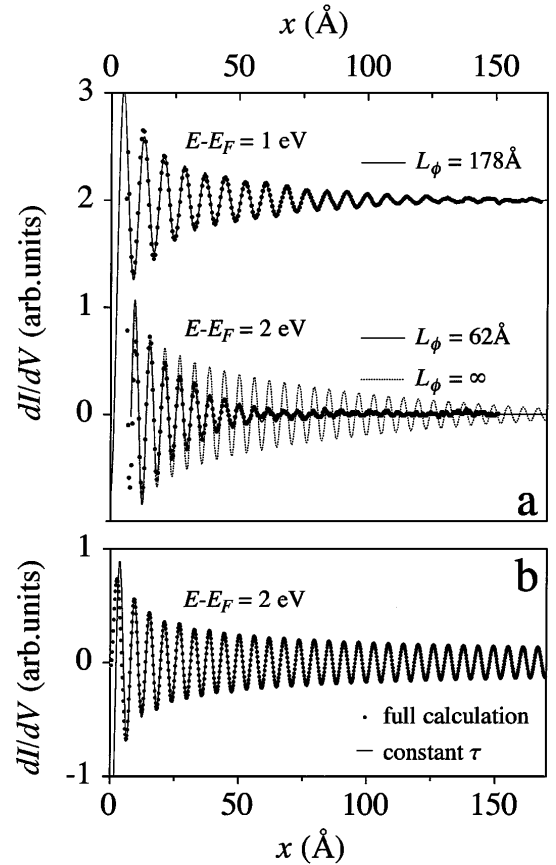
where x is the distance from the step, $k_E = \sqrt{2m^*(E - E_0^{2D})/\hbar^2}$, $L_0 = m^*/(\pi\hbar^2)$ is the density of states of the free 2D electron gas, and ρ_b is the bulk contribution to the surface LDOS. The step reflection amplitude $r(q)$ is a positive real quantity due to the fact that the reflection phase shift is close to $-\pi$ [22]. The $e^{-2(xk_E/qL_\phi)}$ term in Eq. (2) accounts for inelastic scattering processes on the terrace which destroy coherence and thus damp the LDOS oscillations. Numerical integration of Eq. (2) shows that for $x > \pi/k$ and a reasonable energy dependence of r [22,23], ρ_s can very well be approximated by

$$\rho_s(E,x) \approx \rho_b + L_0 \left[1 - r(k_E)\, e^{-2(x/L_\phi)}\, J_0(2k_E x)\right], \tag{3}$$

which is exact for $L_\phi = \infty$. Note that even in the absence of inelastic scattering ($L_\phi = \infty$) the LDOS oscillations at a step edge decay with $1/\sqrt{x}$, since J_0 does. With Eqs. (1) and (3) we have calculated dI/dV numerically, using the constant current tip sample distance 5 Å $+ z(x)|_{I,V}$ of Ref. [20], and typical 5 K parameters for the Cu(111) and Ag(111) surface states [8,9,18,20]. The result of such a calculation is depicted in Fig. 2(b) (dots) and compared with the result obtained by setting the transmission factor $\mathcal{T}$ constant (full line). From plots as shown in Fig. 2(b) it is clear that the energy and gap width dependence of the transmission factor is not responsible for a faster decay of the oscillations in dI/dV at steps (at least not in the bias regime of 0.5–3.5 V). For the sake of a faster fit procedure we have discarded the transmission factor $\mathcal{T}$ altogether, which is an excellent approximation for $x > \pi/k$ and $0.5\ \text{V} < V < 3.5$ V [see Fig. 2(b)]. Under these circumstances the integral in Eq. (1) with ρ_s from Eq. (3) can be solved, and the laterally varying part of the current, $I^\sim$, is given by [20]:

$$I^\sim(V,T,x) \propto -\frac{1}{x}\, e^{-(2x/L_\phi)}\Bigg[\frac{\xi_{k_{eV}}}{\sinh\xi_{k_{eV}}}\, k_{eV} J_1(2k_{eV}x)$$
$$-\frac{\xi_{k_F}}{\sinh\xi_{k_F}}\, k_F J_1(2k_F x)\Bigg], \tag{4}$$

where J_1 is the first order Bessel function and $\xi_k = x\frac{2\pi m^*}{\hbar^2}\frac{k_B T}{k}$. Since we have measured our dI/dV data with a considerable bias modulation ΔV we do not fit our data with the real derivative of Eq. (4), but with its lock-in derivative given by

$$dI/dV(V, \Delta V) \propto \int_0^{2\pi} \sin(t) \cdot I\left[V + \frac{\Delta V}{2}\sin(t)\right] dt, \tag{5}$$

where Eq. (4) has to be inserted for the current I. Note that in the limit of $\Delta V \to 0$ the lock-in output of Eq. (5) coincides with the real derivative. By using Eqs. (4) and (5) to fit our data we take fully account of modulation and temperature effects. The bias modulation actually leads to an additional decay in dI/dV with a decay length $L_{\Delta V}$ of the order of $L_{\Delta V} \sim \hbar^2 k_{eV}/(m^* e\, \Delta V)$. We are left

with four fit parameters: L_ϕ, k_{eV}, the step edge location, and an overall proportionality factor. Note that the latter fully accounts for loss of coherence during the scattering process at the step edge itself [$r(q)$ in Eq. (2)] whereas the decay L_ϕ is influenced only by inelastic processes on the terrace, e.g., e-e or electron-phonon interaction.

Fits to measured dI/dV data for Cu(111) are depicted in Fig. 2(a) for two different bias values (e.g., injection energies). The fit range has been limited to $x > 3\pi/2k$ to ensure the validity of our approximations. The agreement between fits and data is excellent and the relevance of L_ϕ is demonstrated by plotting the calculated dI/dV oscillations for $L_\phi = \infty$. By fitting dI/dV data taken at different bias voltages V (i.e., energies eV) for Ag(111) and Cu(111) we obtain the dispersion relation $k_{E=eV}$, and the energy dependent phase relaxation length $L_\phi(E)$ for Ag(111) and Cu(111), respectively. The fitted k_E values agree well (within 10%) with the 5 K dispersion relations determined previously [20] and reported in Refs. [8–10,18], where $E_0^{2D} = -65$ meV, $m^* = 0.40\, m_e$ for Ag(111) and $E_0^{2D} = -420$ meV, $m^* = 0.40\, m_e$ for Cu(111).

To compare our results with theory, APS, and 2PPE measurements we have converted the measured L_ϕ into lifetimes τ_ϕ via $\tau_\phi = L_\phi/v$, where $v = \hbar k_{eV}/m^*$ is the group velocity. This conversion is correct since $L_\phi < L_m$ in our case [1]. The measured $\tau_\phi(E)$ are shown in Fig. 3 for Ag(111) and Cu(111). The points in Fig. 3 have been determined by averaging over data sets obtained with different tips, at different step edges and different fit ranges [24]. The fit range and bias modulation dependence of our τ_ϕ data is minor, and the error bars are
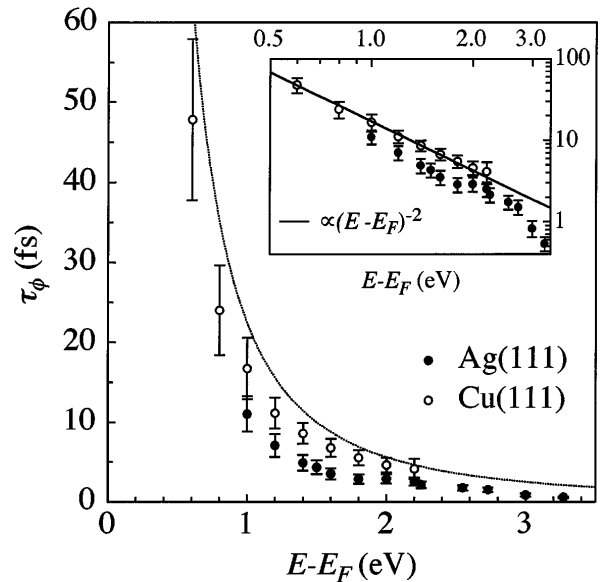

FIG. 3. Lifetimes of surface state electrons as a function of excess energy determined as described in the text. The dotted line depicts the lifetimes predicted by 3D FLT for Cu [25]: $\tau = (22.4\ \text{fs eV}^2)(E - E_F)^{-2}$. The inset shows the same data on a double logarithmic scale. The best inverse quadratic fit to the Cu data yields $\tau = (17.1\ \text{fs eV}^2)(E - E_F)^{-2}$ (full line).

due to a slight tip dependence of our measurement and a 5% uncertainty in the STM piezo calibration. Actually, the absolute values of the lifetimes have been found to depend slightly on the tip, whereas the energy dependence of $\tau_\phi(E)$ is unaffected. This might be explained by the fact that real tips are not radially symmetric and thus may collect surface state electrons having different in-plane incidence angles $\alpha = \arccos(q/k_{eV})$ with different probabilities. Thus, the integrand in Eq. (2) would have to be multiplied with a probability function $f(q/k_{eV})$. It turns out that a monotonically increasing (decreasing) $f(q/k_{eV})$ leads to a slower (faster) decay of ρ_s.

Note that with our technique we avoid depopulation and cascade effects present in 2PPE, and with a tunneling current of typically 10 nA we inject an electron about every 16 ps (i.e., $\gg \tau_\phi$), and so we probe only one excited electron at a time. Since electron-phonon lifetimes are essentially independent of the quasiparticle energy for the energies of interest, and with typically 70 fs at 5 K exceed our measured lifetimes considerably [10], we attribute the inelastic quasiparticle scattering rate τ_ϕ^{-1} to e-e interaction, i.e., electron-hole pair creation and plasmon excitation. Although surface state electrons are bound to two dimensions they coexist with the underlying bulk electrons, and this opens up fully 3D decay channels, e.g., the e-e interaction is not restricted to the 2D electron gas itself but may have contributions from the bulk electrons. Since the bulk k_F^{3D} exceeds the surface state k_F^{2D} by about a factor of 10, screening due to bulk electrons happens on a much shorter length scale than screening by surface state electrons, and hence the 3D contribution to the e-e scattering may be considerable. The fact that the surface state LDOS oscillations measured with STM can perfectly be explained with the simplest model neglecting Coulomb interaction [18–20,22] is direct evidence for the strong screening effect of the bulk electrons. Our τ_ϕ for Ag(111) in Fig. 3 is comparable to previously reported 2PPE results for bulk electrons from polycrystalline Ag [13]. For Cu(111) *bulk* electrons there exist two 2PPE studies: Hertel *et al.* [14] report lifetimes that lie close to our values, whereas Ogawa *et al.* [16] found a factor of 3–4 larger lifetimes. In addition our lifetimes follow the $\lambda (E - E_F)^{-2}$ law predicted by 3D FLT for electron hole pair creation [25,26]: Fits to our data yield $\lambda_{Ag} = 10.4$ fs eV^2 and $\lambda_{Cu} = 17.1$ fs eV^2, as compared to 16.5 fs eV^2 and 22.4 fs eV^2 expected from FLT for Ag and Cu parameters, respectively (see Fig. 3). We therefore believe that our measured phase relaxation times of surface state quasiparticles are governed by inelastic e-e scattering with 3D bulk electrons. Two possible explanations can be thought of to explain why our lifetimes are smaller than predicted by FLT: The FLT

cited above disregard the real electronic band structure [16], and, secondly, the in-plane e-e interaction of the surface state may contribute to the scattering rate and thus reduce the lifetimes.

Finally, we would like to emphasize the possibility to study bulk quasiparticle lifetimes with STM much as described here, since bulk electrons create standing wave patterns at structural defects on surfaces as well.

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[24] We point out that the absence of an influence of the tunneling impedance on our measurement has been carefully checked by measuring L_ϕ at fixed bias and a stabilizing current that has been varied by a factor of 100 around the usual values. Thus, the presence of the tip, i.e., the tip induced electric field or tip-surface interactions, does not influence the measured decay lengths.

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