Inelastic Tunneling Excitation of Tip-Induced Plasmon Modes on Noble-Metal Surfaces

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Light emission characteristics from the tunnel gap of a scanning tunneling microscope are used to elucidate the interaction of tunneling electrons with tip-induced plasmon modes on Ag, Au, and Cu surfaces. Enhanced redshifted spectra are observed in the tunneling regime. Model calculations of optical spectra in this range agree well with the experimental data. Isochromat spectra are used to demonstrate that the principal excitation process occurs via inelastic tunneling.

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An electron traversing a vacuum-metal interface has a significant probability of interacting with collective electron oscillations. In the scanning tunneling microscope (STM) the interaction of tunneling electrons with collective electromagnetic modes and the coupling of these modes to photons are phenomena of fundamental interest and, as will be demonstrated, provide a unique probe for tip-surface interactions involving inelastic electron tunneling (IET) excitation of local plasmon modes. Light emission from metal-oxide-metal (MOM) sandwich junctions containing Au or Ag was observed many years ago [1,2]. There the role of IET versus hot electron excitation of radiative plasmon modes remains controversial despite much theoretical effort [1–5]. More recently we proposed that local plasmons were responsible for the observation of enhanced photon emission (10^{-3}–10^{-4} photons/electron) from the tunnel junction of an STM operating on rough polycrystalline silver films [6–9]. Many of the experimental limitations inherent with MOM junctions can be overcome using the STM as a local excitation source on well-defined surfaces.

In this Letter we shall present the first experimental evidence and model calculations of photon emission from low-index single-crystal surfaces of Ag(111), Au(110), and Cu(111) excited using the STM in the tunnel and field emission modes. As will be shown, tunneling electrons interact strongly with charge-density oscillations confined between the tip and surface. Because of a loss of translational invariance introduced by the proximity of the tip, conversion of these modes into photons is facilitated, enabling observation of their energy distribution. An analysis of photon emission and tunneling spectroscopic data is used to identify IET as the dominant excitation mechanism coupling the tunneling electrons to local electromagnetic modes.

The measurements were conducted in a vacuum chamber with a base pressure of 5×10^{-11} Torr. The experimental setup was described in detail elsewhere [10]. Au(110), Cu(111), and Ag(111) single crystals were prepared by repeated cycles of sputtering and annealing and characterized by LEED, STM, and x-ray photoemission spectroscopy. In this study etched W tips heated in UHV to 1000 °C and then sharpened by Ne-ion bombardment were used. Extended defect-free regions showing the (1×2) reconstruction of the Au(110) surface [11] and the (1×1) atomic configuration for Cu(111) and Ag(111) were routinely obtained.

Figure 1 displays the integral photon intensity from Ag(111) in the wavelength range 350–750 nm as a function of V_t recorded at constant current [12]. Similar spectra were observed for Au(110) and Cu(111). Significant photon emission was observed in two distinct ranges of tip bias voltage V_t separated by a characteristic drop in intensity reaching a minimum at $V_t \sim 100$ V. In the *field emission* regime electron emission is essentially determined by the enhanced electric field at the tip resulting in a propagating electron impinging on the surface. Transition radiation due to the collapsing image dipole and also roughness-coupled emission from excited surface plasmons similar to electron-beam experiments are induced [13]. The emission from these processes is known to decrease at lower electron energies in agreement with our observations at $V_t > 100$ V in Fig. 1. Corresponding pho-

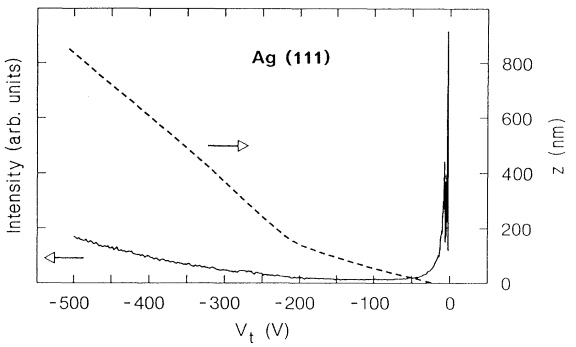

FIG. 1. Integral photon yield from Ag(111) in the wavelength range 350–800 nm [12] as a function of tip bias voltage V_t. The STM was operated in constant current mode ($i_t = 1$ nA). The dashed line shows the simultaneously recorded tip excursion.

ton emission spectra are shown in Fig. 2 (top row) [14]. For Ag emission peak A is assigned to radiation from surface and bulk plasmons at 3.69 eV [15] and 3.76 eV [13] known from electron-energy-loss spectroscopy (A' is a second-order Bragg peak of A). The features in the Au spectra [2.4 eV (B)] and Cu spectra [4.3 eV ($C1$), 2.5 eV ($C2$), and 2.1 eV ($C3$)] are attributed to fluorescence and agree with the energy of the transitions $L_3(Q_+) \rightarrow E_F(L_2')$ (B,$C3$), $L_3(Q_-) \rightarrow E_F(L_2')$ ($C2$), and $X_5 \rightarrow X_4'$ ($C1$) [16].

At lower values of V_t in what we term the *proximity-field emission* ($|V_t| \lesssim 50$ V) and tunneling regimes ($|V_t| \lesssim 4$ V) where the wavelength of visible light is much longer than the gap spacing (see dashed line in Fig. 1 showing the corresponding tip excursion during the voltage ramp), the photon intensity is observed to increase rapidly, exhibiting a series of oscillations with the highest signal intensity in the tunneling regime. Spectra obtained in both tunnel and proximity-field emission modes for Ag, Au, and Cu consistently show the main emission peak shifted to longer wavelengths (see middle row of Fig. 2). Such peaks are detected at 2.0 eV (E,F) for Au and Cu and at 2.4 eV (D) for Ag. For a series of voltages we find that the low wavelength limit follows the expected quantum cutoff $\lambda_c = hc/eV_t$; however, for $V_t \gtrsim 3$ V the peak positions are almost invariant with respect to excitation voltage. This observation and the high intensities indicate a resonantly enhanced inelastic process.

We use the theory of Johansson, Monreal, and Apell [7] to calculate spectra of spontaneous emission from an STM tip close to flat for Ag, Au, and Cu surfaces. The classical electromagnetic response (including plasmon resonances) of a model system where the tip is simulated by a sphere is used to obtain the strength of field fluctuations responsible for spontaneous emission. Given the small radius of the sphere in the model ($R = 300$ Å) retardation effects can be neglected. Experimental dielectric functions were used for tip and sample materials [17]. The high-frequency components of the tunnel current driving the radiation are given by the current matrix elements between inverse-photoemission initial and final states.

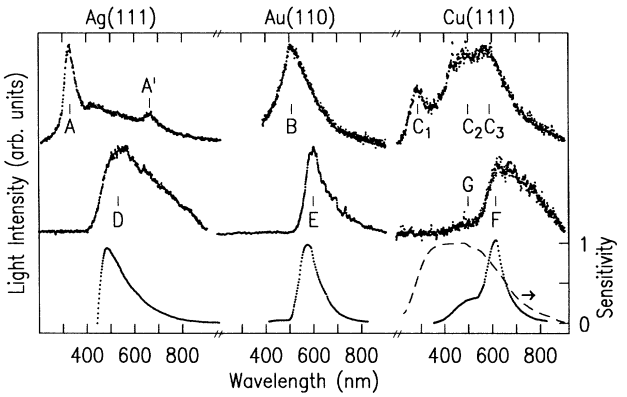

FIG. 2. Optical emission spectra from Ag(111), Au(110), and Cu(111). Spectra in the topmost row were observed in the high-voltage field emission regime. Spectra in the tunnel regime ($V_t = 2.8$, 3.0, 3.6 V, $i_t = 10$, 10, 100 nA) are shown in the middle row. The results of our theoretical calculation for the emission in the tunneling regime using experimental parameters are presented in the bottom row. A tip radius of 300 Å was assumed as suggested by scanning electron microscopic images. The sensitivity of the detection system shown as a dashed line was included in the calculation.

In our model emission is enhanced by a factor of $\sim 10^4$ compared with UV inverse photoemission. The enhancement can be understood by the visualizing formation of a tip-induced plasmon (TIP) localized to the region between tip and sample where energy is lower than that of a propagating plasmon mode. Figure 2 (bottom row) shows the resulting spectra calculated with experimental values of the tunnel voltage and currents as input parameters. Good agreement between experiment and theory in the energy position of the maxima and in signal intensity provides persuasive evidence that TIP modes dominate in the emission process. They are analogous to the symmetric or antisymmetric charge-density oscillations observed in attenuated total reflection studies of two metal-dielectric interfaces in close proximity [18]. The electric field of the latter mode, which is primarily confined in the gap region, splits off towards lower energy with decreasing separation between the surfaces.

For a model system with free-electron metal electrodes our analysis shows that the frequency ω_c of the TIP mode is sensitive to the size of the cavity formed between the tip and the sample, i.e., ω_c depends on the radius of curvature of the tip [4]. Given that the dielectric properties of Ag over the photon energy range 2–3 eV are quite free-electron-like, the predicted position of the emission peak is sensitive to tip geometry. In contrast, for Au and Cu calculations for different tip radii indicate that ω_c is relatively insensitive to tip geometry. This behavior results from the dielectric function of Au and Cu where TIP resonances are found to occur in the energy range of the $L_3(Q_+) \rightarrow E_F(L_2')$ interband transitions at 2.4 and 2.1 eV, respectively. These transitions produce a rapid variation of the real part of the dielectric function over a narrow energy range. Our observations show some variation in spectral structure during consecutive experimental runs for Ag, but only small shifts of the peak position for Au or Cu, further supporting our explanation. As shown in Fig. 2 both the experimental and the calculated spectra display a rather sharp cutoff in this energy range at low wavelengths; and for Cu a weak shoulder (G) is also reproduced by the calculation.

The excitation mechanism of these TIP modes by tunneling electrons is particularly interesting since it involves interaction of electron tunneling events with local electromagnetic modes. A comparison of the respective con-

tributions to the matrix elements in our calculation clearly favors IET for the STM experiment on flat surfaces and *predicts no significant polarity dependence in spectral features and intensities* except subtle changes in the spectra due to differences in the static potential barrier. An analogous result was obtained previously within the model of Persson and Baratoff [8]. Experimentally we observe similar spectral features and intensities with both polarities of V_t supporting IET but contradicting a hot electron picture where excitation occurs within a mean free path of the material. In STM it is, however, possible that a layer of sample material on the tip, with a thickness comparable to the inelastic mean free path, would give rise to emission at V_t positive in a hot electron model. However, optical spectra recorded for Ag and W tips purposely coated with a thick Ag layer ($\sim$1000 Å) display markedly different characteristics from the data presented here. In qualitative agreement with our model for an Ag tip against an Ag surface, multiple peaks and a decrease in emission line width are observed permitting us to discard the "coating" hypothesis.

It is important to include additional tests for an IET mechanism. This can be obtained from a comparison of differential conductance (dI/dV) tunneling spectra with simultaneously recorded isochromat photon yield spectra ($\lambda = 600$ nm) in the constant current mode for values of V_t corresponding to *proximity-field* emission. Here, oscillatory behavior is observed in dI/dV at $V_t > -5$ V corresponding to constructive-destructive interference of electron standing waves [19]. Interestingly, isochromat spectra also exhibit similar oscillatory behavior. Figure 3 shows a plot of the maxima in dI/dV versus the neighboring peak in photon yield. The intercept at $V_t = 2.2$ eV close to the isochromat energy $h\nu = 2.07$ eV [20] clearly supports the interaction of the tunneling electrons to TIP modes via an IET mechanism: For IET, the probability of elastic tunneling depends on the local density of states on the collector at an energy $\sim h\nu$ below E_F of the emitter.

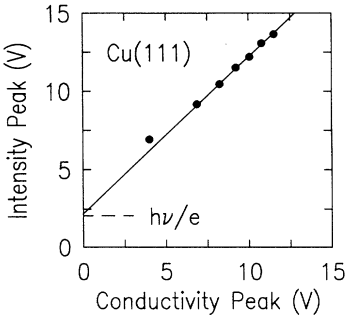

FIG. 3. Positions of peaks (above $V_t = 5$ V) of light emission intensity at $\lambda = 600$ nm vs positions of peaks in conductivity recorded simultaneously on a Cu(111) surface. The experimental data are fitted by a straight line with slope 1 and intercept 2.2 V. The position of the lowest peak was not included in the fit [20].

This implies, in a constant static field approximation, that the maxima in tunneling and photon spectra are separated by a quantum of energy ($-h\nu$) as found in Fig. 2. For hot electron excitation one expects electron injection and ballistic transport processes to be relatively insensitive to the matching conditions of the tip and surface wave functions under conditions of constant elastic current with a possible energy-dependent branching ratio of current flow to surface states versus injection into the bulk. The latter effect would result in a phase shift in the peak positions but not a constant offset as observed.

Figure 4 shows photon maps and simultaneously acquired topographies at $V_t = -3.8$ V, $i_t = 5$ nA from a Cu(111) surface consisting of terraces separated by monatomic steps and a line of small structures $\sim$2 Å in height and $\sim$20 Å in diameter. These structures were fabricated by pulsing the applied electric field at positive tip bias [21]. In the photon map [Fig. 4(b)] both atomic steps and the structures are observed to give lower photon intensities. The contrast mechanism occurs on a near atomic scale. Two factors can produce local variations in photon intensity: First, photon maps recorded at constant tunnel current reflect local changes in both coupling and the field distribution of TIP modes giving rise to long-range variations particularly on rough granular films and metallic islands [22]. Additionally, the ratio of inelastic/elastic tunneling probabilities, which is expected to be sensitive to atomic configurations such as steps or foreign adsorbate structures, may introduce a short-range con-

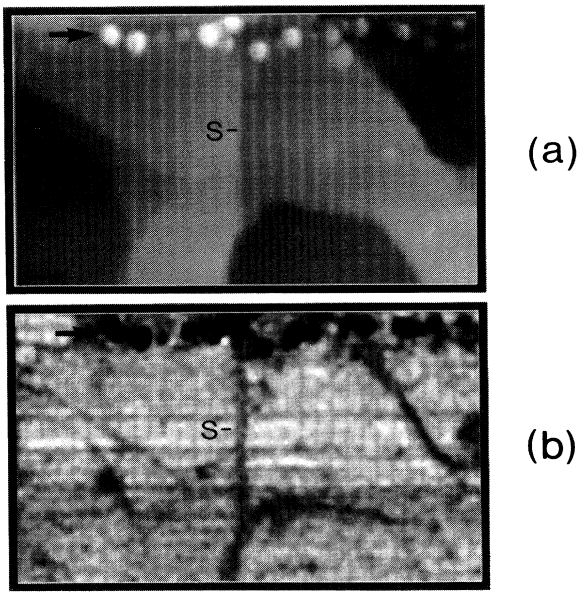

FIG. 4. (a) Constant current topography and (b) photon STM images of a Cu(111) surface exhibiting terraces separated by steps and small structure, indicated by arrows, created by a series of electric-field pulses at positive tip polarity. Images recorded simultaneously at $V_t = -3.5$ V, $i_t = 2$ nA. Area = 500 Å × 300 Å.

trast mechanism spatially limited by the excitation volume consistent with the variations in photon intensity shown in Fig. 4(b).

In summary, we have shown that the proximity of a tip to the surface in STM can create tip-induced localized plasmon modes which interact strongly with tunneling electrons. Clear evidence that this interaction occurs via inelastic tunneling is presented. Good agreement between a theoretical analysis and experimental optical spectra is found for the tunnel regime. We provide evidence that photon emission from the STM contains useful information on a subnanometer scale of the interaction of tunneling electrons with spatially confined electromagnetic modes.

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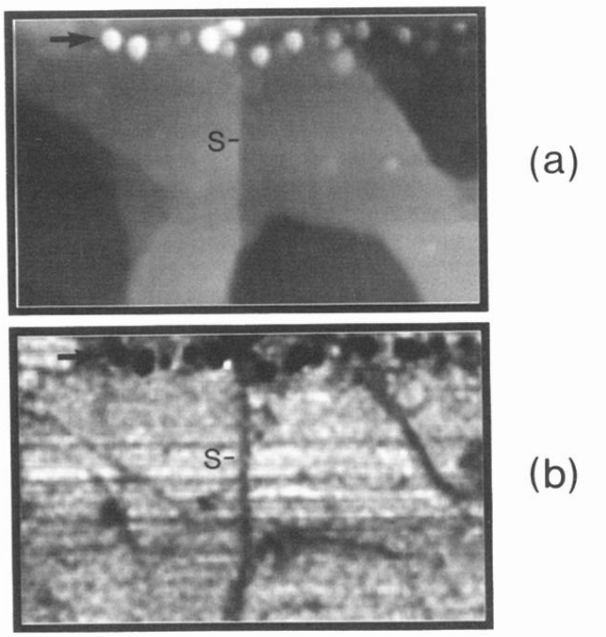

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