Two-Electron Photon Emission from Metallic Quantum Wells

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Unusual emission of visible light is observed in scanning tunneling microscopy of the quantum well system Na on Cu(111). Photons are emitted at energies exceeding the energy of the tunneling electrons. Model calculations of two-electron processes which lead to quantum well transitions reproduce the experimental fluorescence spectra, the quantum yield, and the power-law variation of the intensity with the excitation current.

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Tunneling electrons in a scanning tunneling microscope (STM) can excite vibrational or electronic modes of the sample by inelastic tunneling provided that their energy exceeds the excitation energy. These excitations have been detected either by their contribution to the tunneling current [1] or by investigating light that is being emitted from the tunneling gap [2,3]. Thus, inelastic tunneling spectroscopies have been performed. Usually, tunneling electrons can safely be assumed to be independent of each other in these spectroscopies. Even at a high tunneling current $I = 100$ nA the average time between two consecutive tunneling events is ~ 1.6 ps. Assuming Poisson statistics, two electrons are rather unlikely to interact in the tunneling gap. As a consequence, inelastic processes which involve multiple electrons have been observed only in the particular case of STM-induced desorption of H from Si. The lifetime of the H-Si stretch mode which is involved in desorption is in the range of nanoseconds [4] enabling an interaction with several consecutive electrons before deexcitation.

Here, we report on unusual emission of visible light from Na on Cu(111), a metallic system which exhibits well-studied quantum well states (QWS) near the Fermi energy E_F [5–12]. Surprisingly, fluorescence spectra reveal the emission of "forbidden" photons whose energy $h\nu$ significantly exceeds the energy of a tunneling electron eU, where U is the sample voltage. The intensity of the forbidden light increases approximately as $I^{1.5}$, where I is the tunneling current, with the exponent decreasing to 1.2 at the highest currents used. Its quantum efficiency reaches values of up to $\sim 10^{-7}$ photons per tunneling electron at large I.

Since electronic lifetimes at the Na/Cu(111) surface are on a fs time scale [5] we are led to conclude that two-electron processes are involved which do not rely on a stepwise accumulation of energy in an excited mode. We propose a model where two electrons tunnel more or less simultaneously. Once they are in the vacuum-barrier region between tip and sample they may exchange energy through the Coulomb interaction which is relatively unscreened there. As a result of this Auger-like process, one of the electrons can emit a photon with $h\nu > eU$. Despite the simplicity of the model, calculated fluorescence spectra and the current dependence of the quantum efficiencies are comparable to the experimental data.

Spectral structure extending beyond the condition $h\nu < eU$ has been reported for photon emission from Au films investigated at ambient temperature. However, no explanation of this intriguing result is currently available [13]. Uehara *et al.* [14] reported on light emission at $h\nu = 2\,eU$ from superconducting Nb tips and samples at $T = 4.7$ K and explained this emission in terms of Cooper-pair tunneling. Photon emission at large $h\nu$ has also been observed from metal point contacts which emit blackbody radiation at elevated currents [15].

Our experiments were performed with an ultrahigh vacuum (UHV) STM operated at a temperature $T = 4.6$ K [16]. W tips were prepared by electrochemical etching and subsequent sputtering and annealing in UHV. The Cu(111) surface was cleaned by repeated cycles of Ar-ion bombardment and annealing. Na films were evaporated from outgassed SAES Getters sources onto the Cu crystal held at room temperature. Na coverages were calibrated using the binding energies of the lowest QWS [5]. After preparation at room temperature the samples were transferred to the STM and cooled to $T = 4.6$ K. Photons in the energy range $1.1\ \text{eV} < h\nu < 3.5$ eV were detected with a lens system in UHV, coupling the light to a grating spectrometer and a liquid nitrogen cooled CCD camera [17]. The spectra have been corrected for the wavelength dependency of the detection efficiency. For the voltages used, up to currents of ~ 100 nA, surface modifications were rarely observed on flat surfaces. While surface modification becomes more probable at higher currents, during acquisition of the data sets shown here no such events occurred as verfied from STM images and simultaneous monitoring of the vertical tip position.

Figure 1 displays fluorescence spectra recorded at elevated tunneling currents from (a) a 2 ML and (b) a 0.6 ML Na film on Cu(111). The QWS binding energies are known from tunneling spectroscopy [18]. At 2 ML, unoccupied states exist at $E_1 = 0.15$ eV and $E_2 = 2.2$ eV. At 0.6 ML, these states are located at $E_1 = 0.4$ eV and $E_2 = 2.1$ eV. Previously, photon emission due to two processes has been reported from these layers [3,19]. At low U, i.e., $eU < E_2$, electrons tunnel inelastically from the tip Fermi level to the lower QWS and emit photons. Fluorescence spectra reveal a maximum which shifts with eU. When $eU > E_2$, tunneling to the upper QWS occurs and a subsequent transfer of an electron to the lower QWS gives rise to the emission of quantum well luminescence at $h\nu = E_2 - E_1$. Enhancement by a local plasmon renders these processes efficient. The data of Fig. 1 appear to be consistent with this picture. Two spectral components are discernible, an emission at low photon energies involving inelastic tunneling and an additional peak at (a) $h\nu \sim 2.0$ eV and (b) $h\nu \sim 1.7$ eV which is due to transitions between QWS. What is new in Fig. 1 is the fact that these data were recorded at a sample voltage (a) $U = 1.42$ V and (b) $U = 1.80$ V. In Fig. 1(a) the entire quantum well emission peak seems to violate energy conservation $h\nu \sim 2$ eV $> eU$ with a maximum energy excess of $\sim$0.7 eV. In Fig. 1(b) there is still significant intensity with $h\nu > eU$. However, the quantum well emission at $h\nu \sim 1.7$ eV in Fig. 1(b) becomes even more surprising if one recalls that the upper QWS, which is involved in the underlying transition, is located at $E_2 = 2.1$ eV which is substantially larger than eU.

Two-electron processes provide a natural explanation of the unusual emission in Fig. 1. Since such processes imply a nonlinear variation of the intensity with the tunneling current I we recorded series of some 800 fluorescence spectra while varying I and evaluated the forbidden intensity. The double-logarithmic plot in Fig. 2 reveals that the intensity scales approximately like $I^{1.5}$ (at low currents) confirming the above explanation. As a consequence, the forbidden emission is weak at low tunneling currents. That is why it has been overlooked previously. In addition to its variation with I, the intensity of the quantum well emission from 0.6 ML Na also depends strongly on the voltage U for $U < 2$ V. Consequently, the quantum efficiency of the forbidden emission varies significantly depending on the specific I and U chosen. We estimate an efficiency on the order of 10^{-7} photons per tunneling electron at $I = 100$ nA and $U = 1.8$ V from 0.6 ML Na.

A possible explanation of the observed two-electron processes appears to be tunneling of an electron into a long-lived empty state of the Na/Cu(111) surface and subsequent further excitation of this electron via interaction with a second tunneling electron. We estimated the probability of such processes assuming a Poisson distribution of the intervals between tunneling events. To obtain the observed quantum efficiencies an excited electronic state with a lifetime $\tau \approx 1$ ps needs to be postulated. This value is much larger than typical electronic lifetimes at surfaces. Moreover, it is unclear why an electron should remain localized under the tip over this extended period of time. We therefore discard this type of mechanism.

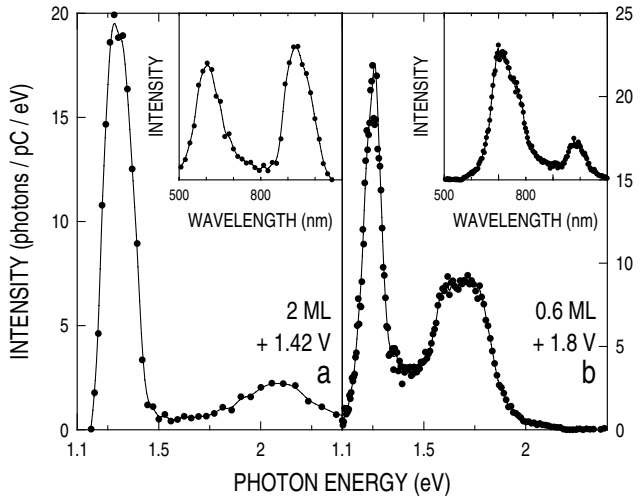

FIG. 1. Fluorescence spectra from Na monolayers on Cu(111). (a) 2 ML Na, $U = 1.42$ V, $I = 100$ nA. (b) 0.6 ML Na, $U = 1.80$ V, $I = 357$ nA. Solid lines serve to guide the eye. The data have been corrected for detector response. However, due to uncertainties of the rapidly decreasing detector sensitivity at photon energies below $\sim$1.25 eV the correction is reliable only at higher photon energies. The insets show the uncorrected data as measured (in counts vs wavelength in nm).

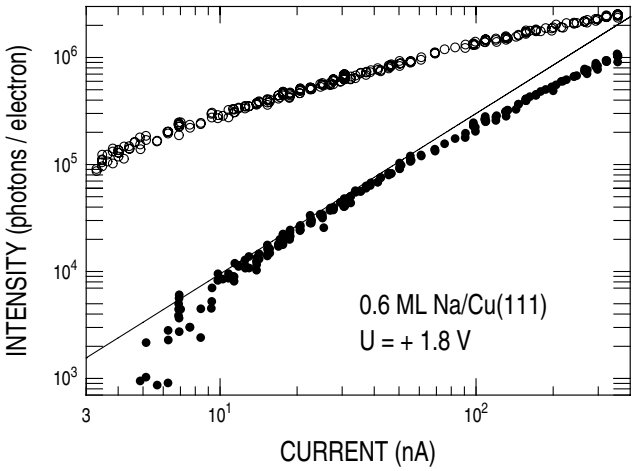

FIG. 2. Intensity of quantum well emission (dots, 1.45 eV $< h\nu <$ 2 eV, corrected for detection efficiency) and emission due to inelastic tunneling (circles, 1.1 eV $< h\nu <$ 1.45 eV) vs current I evaluated from 830 fluorescence spectra of a 0.6 ML coverage at $U = 1.8$ V. As a guide to the eye a slope of $I^{1.5}$ is indicated (line).

We have instead considered two other two-electron mechanisms that we believe cause emission of photons with an energy exceeding eU: (i) a coherent Auger-like process in which energy is transferred from one tunneling electron to another and (ii) decay of the hot holes [20] that are injected into the tip because most of the tunneling current passes through the lower QWS. The decaying holes create hot electrons in the tip which subsequently can tunnel into the upper QWS and thereby cause photon emission.

The Keldysh Green's function (GF) formalism provides a suitable theoretical framework for calculating the intensity of the emitted light from a system out of equilibrium such as an STM under finite bias. The intensity can be written [19]

$$\frac{dP}{d\Omega d(\hbar\omega)} = \frac{\omega^2|G(\omega)|^2}{16\pi^3\epsilon_0 c^3\hbar}\int_V d^3r\int_V d^3r' i\Pi^<(\vec{r},\vec{r}',\omega). \tag{1}$$

The integrations run over a volume between the tip and sample where the electrons and photons interact efficiently. G is a factor describing the enhancement of the electromagnetic vacuum fluctuations in the tip-sample cavity, and $\Pi^<$ is the Fourier transform of the current-current GF, $-i\langle j_z(\vec{r}',0)j_z(\vec{r},t)\rangle$, which in the case of *allowed* light emission can be expressed in terms of a current matrix element between the initial and final electron states [19]. The detailed calculations of electron states and matrix elements employ a one-dimensional model for the system. The Cu potential is corrugated to yield a band gap of 5 eV at the Brillouin zone boundary, while the potential in the Na layer and the tip are assumed to be constant [21]. A tilted square barrier, rounded and lowered by image-potential contributions, separates the electrodes. In addition, the potential in the Na layer is given an imaginary part $-i\Gamma$, with $\Gamma = 0.1$ eV, to mimic the electron scattering processes that limit the lifetime of the quantum well states.

For *forbidden* light emission through an Auger-like process, the leading contribution to the integrals in Eq. (1) can be written in terms of a sum of the squares of second-order matrix elements,

$$\frac{dP}{d\Omega d(\hbar\omega)} = \frac{\omega^2|G(\omega)|^2}{8\pi^2\epsilon_0 c^3}\sum_{k_1k_2q}|M_{k_1,k_2,q}|^2\delta(E_{k_1}+E_{k_2}-E_{1,k_1+q}-E_{1,k_2-q}-\hbar\omega). \tag{2}$$

$M_{k_1,k_2,q}$ describes how two electrons in the tip labeled by the momenta $\vec{k}_1$ and $\vec{k}_2$ first interact through a screened Coulomb interaction, $e^2e^{-\kappa|\vec{r}_1-\vec{r}_2|}/(4\pi\epsilon_0|\vec{r}_1-\vec{r}_2|)$, and exchange energy and momentum [22]. One electron goes into the lower QWS [with in-plane momentum $\vec{k}_{1,\parallel}+\vec{q}$ and energy $E_{1,k_1+q} = E_1 + \hbar^2(\vec{k}_{1,\parallel}+\vec{q})^2/(2m)$] directly and takes no further part in the process, while the other eventually emits a photon in a transition from an intermediate state into the lower QWS (with in-plane momentum $\vec{k}_{2,\parallel}-\vec{q}$ and energy E_{1,k_2-q}). When the two electrons have opposite spin we can write

$$M_{k_1,k_2,q} = \frac{-ie\hbar}{2m}\int_V d^3r\int_V d^3r_1\int_V d^3r_2\left\{\phi^*_{k_2-q}(\vec{r})\frac{\partial g^r}{\partial z}(\vec{r},\vec{r}_2) - \frac{\partial\phi^*_{k_2-q}}{\partial z}g^r(\vec{r},\vec{r}_2)\right\}\phi^*_{k_1+q}(\vec{r}_1)\frac{e^2e^{-\kappa|\vec{r}_1-\vec{r}_2|}}{4\pi\epsilon_0|\vec{r}_1-\vec{r}_2|}\psi_{k_2}(\vec{r}_2)\psi_{k_1}(\vec{r}_1), \tag{3}$$

where ϕ denotes the QWS wave function, while ψ stands for tip wave functions. The retarded electron Green's function g^r describes the propagation of the electron in the intermediate state before photon emission. For energy and momentum conservation to hold in the photon emission process the energy and in-plane momentum in the intermediate state must be $E_{1,k_2-q}+\hbar\omega$ and $\vec{k}_{2,\parallel}-\vec{q}$, respectively. The electron Green's function has a resonance when its energy argument coincides with the energy of the upper QWS which explains why, as we will see, the forbidden light emission mainly produces photons with energy $h\nu = E_2 - E_1$.

We have also calculated the light emission intensity as a result of hot-hole decay. To this end we studied a semiclassical model based on Ref. [23] for hot-hole-electron cascade and diffusion (with an elastic mean free path of 2 nm) in the tip and calculated the influx of secondary hot electrons onto the tip apex. This influx was then used as input in a calculation of the light emission intensity along the line of Ref. [19].

Figure 3 displays results from our model calculations obtained for $U = 2$ V and $I = 10$, 100, and 300 nA, respectively. The model potential leads to $E_1 = 0.2$ eV and $E_2 = 2.5$ eV at $U = 2$ V. Under these conditions, the upper quantum well state at E_2 is not accessible. Moreover, the energy eU of a single electron is not sufficient for exciting the corresponding quantum well transition. As a result, one-electron processes (solid lines in Fig. 3) give rise to plasmon mediated emission by inelastic tunneling from the tip Fermi level only to the lower QWS. The emission occurs predominantly at $h\nu < eU - E_1$ as expected [3,19].

The emission calculated for the Auger-like and hot-hole processes, respectively, are indicated by dashed lines. We do find sizable emission, which is about 1 order of magnitude stronger for the Auger process than for the hot-hole mechanism, peaked at $h\nu \sim 2.3$ eV (thus $h\nu > eU$) due to quantum well transitions. The electron that eventually causes the light emission gains enough

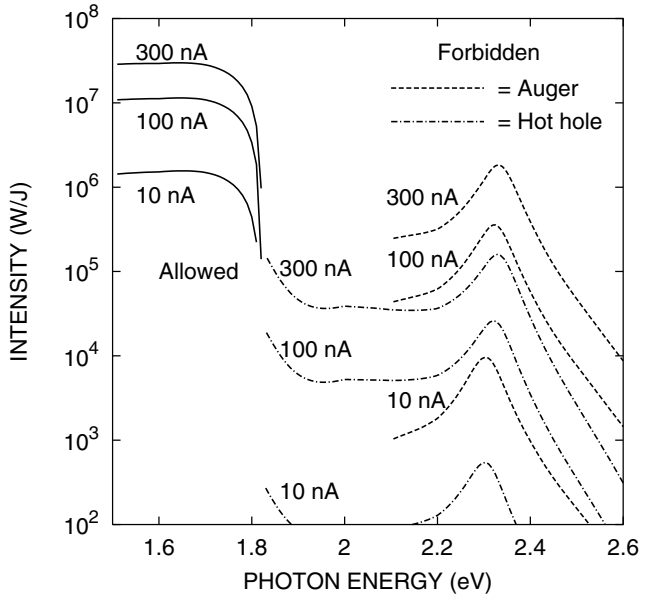

FIG. 3. "Allowed" and "forbidden" light emission calculated for a model system with QWS at $E_1 = 0.2$ eV and $E_2 = 2.5$ eV. Results are shown for the various currents indicated and a voltage $U = 2$ V. The thickness of the Na overlayer was set to 0.613 nm, corresponding to 2 monolayers.

energy (i.e., ≈ 0.5 eV), either through Coulomb interactions with another electron while tunneling, or in the hot-hole-electron cascade in the tip, to be promoted to the upper quantum well resonance situated above the tip Fermi level in energy. We note that the particular electronic structure of Na on Cu(111) with states at well-defined energies is essential in achieving significant signal levels.

The calculations predict quantum yields of up to 10^{-7} photons per electron for the Auger-like mechanism at $I = 100$ nA and $U = 2.3$ V in reasonable agreement with the experimental value. Given the experimental uncertainty of absolute photon intensities, as well as the approximations involved in the calculations, a comparison of its variation with I is more significant. The Auger-like process yields $I^{1.5}$ close to the experimental data. The hot-hole process gives a slightly larger exponent, 1.6. While both mechanisms must be considered as plausible explanations for the forbidden light emission the larger calculated intensities indicate that the Auger process is the dominating one.

In summary, we reported on unusual STM-induced photon emission from a metallic quantum well system at photon energies exceeding the limit $h\nu \leq eU$. Model calculations revealed that owing to the particular electronic structure of Na on Cu(111) two-electron processes can cause quantum well transitions and corresponding fluorescence. Similar effects may be observable in other quantum confined systems.

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