Tunneling from localized surface states of semiconductor with Coulomb correlations

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The time-dependent problem of the tunneling from surface states of a semiconductor localized near the tip of a scanning tunneling microscope is analyzed. The Coulomb repulsion of the electrons in these states is taken into account. The average value of the tunneling current over a long time is derived. The relative fluctuations in this current are estimated. The conditions for experimentally observing this behavior are examined. The possibility of a tunneling spectroscopy of surface states in a dc regime is examined.

In research on the surfaces of semiconductors by scanning tunneling microscopy and spectroscopy, localized surface states have a strong influence on the image obtained experimentally.[1–3] Such states may be caused by "dangling" bonds localized at the surface, by adsorbed atoms and molecules, and by various structural defects. In the present letter we show that in tunneling spectroscopy of semiconductor surfaces it is also necessary to consider time-varying effects associated with either an emptying of surface states localized near the tip of the scanning tunneling microscope or a filling of these states as the result of various processes (scattering, surface diffusion, etc.), particularly if the energies of these states lie in the band gap of the semiconductor.

We consider the situation in which ϵ_j—the energy of a surface state localized near site j—lies in the middle of the band gap. If the width of the gap satisfies $E_c - E_v \sim 1$ eV (this relation holds for Si and many other semiconductors), we can assume $E_c - E_v \gg T$, $T \gg \Gamma_t$, and $|E_{c(v)} - \epsilon_j| \gg T \gg \Gamma_t$, where T is the temperature, and Γ_t is the broadening of level ϵ_j due to tunneling between the sample and the tip. At a current ~ 1 nA, we would have $\Gamma_t^{-1} \sim 10^{-10}$ s and $T \sim 25 \times 10^{-3}$ eV. For such surface states, the relaxation times of the electron density associated with inelastic transitions into the valence band and the conduction band are long:[6] $\gamma^{-1} \sim 10^{-2} - 10^{-4}$ s.

The primary mechanisms for the filling of these states, localized near the tip of the scanning tunneling microscope, are electronic transitions between neighboring sites, i.e., quantum surface diffusion. The Coulomb repulsion (U) of electrons with opposite spins which are localized at a common site becomes important in this case[1] (Refs. 4 and 5).

We assume $\epsilon_j < E_F$ and $V_s < 0$, i.e., that the voltage across the sample is negative.[2]

To describe this system, we use the Hamiltonian

$$\hat{H} = \sum_{k,\sigma} \epsilon_k b^+_{k\sigma} b_{k\sigma} + \sum_{j,\sigma} \epsilon_j a^+_{j\sigma} a_{j\sigma} + U \sum_j n_{j\sigma} n_{j-\sigma}$$

$$+ \sum_{jj'} t_{jj'} a^+_{j'\sigma} a_{j\sigma} + \sum_{j,k,\sigma} \delta_{ij} V_{kj} (a^+_{j\sigma} b_{k\sigma} + b^+_{k\sigma} a_{j\sigma}), \qquad (1)$$

where $b^+_{k\sigma}$ and $a^+_{j\sigma}$ are operators which create an electron in the states (k,σ) and (j,σ) in the tip and in the sample, respectively, $\epsilon_{k\sigma}$ and $\epsilon_{j\sigma}$ are the energies of the electrons in these states, U is the energy of the Coulomb repulsion, $t_{jj'}$ is the amplitude of the transition between sites j and j', which differs from 0 only for nearest neighbors, and V_{kj} is the matrix element for a tunneling between states (j,σ) and (k,σ). It is assumed that the tip is above site i and that we have $V_{kj} = 0$ for $i \neq j$. To calculate the tunneling current, we work from a system of kinetic equations for $\langle n_{j\sigma} \rangle$ and $\langle n_{j\sigma} n_{j-\sigma} \rangle$:

$$\frac{\partial}{\partial t} \langle n_{j\sigma} \rangle = \delta_{ij} \sum_k V^2_{kj} [f_{k\sigma} \langle (1-n_{j\sigma})(1-n_{j-\sigma}) \rangle - (1-f_{k\sigma}) \langle n_{j\sigma}$$

$$\times (1-n_{j-\sigma}) \rangle] \delta(\epsilon_j - \epsilon_{k\sigma}) + \sum_{\langle jj' \rangle} \int d\epsilon_j \nu_j(\epsilon_j) \nu_{j'}(\epsilon_j) |t_{jj'}|^2$$

$$\times [\langle n_{j'\sigma} (1-n_{j'-\sigma})(1-n_{j\sigma})(1-n_{j-\sigma}) \rangle - \langle n_{j\sigma} (1-n_{j-\sigma})$$

$$\times (1-n_{j'\sigma})(1-n_{j'-\sigma}) \rangle] + \delta_{ij} \sum_k V^2_{kj} [f_{k\sigma} \langle (1-n_{j\sigma}) n_{j-\sigma} \rangle - (1$$

$$- f_{k\sigma}) \langle n_{j\sigma} n_{j-\sigma} \rangle] \delta(\epsilon_j + U - \epsilon_{k\sigma}) + \sum_{\langle jj' \rangle} \int d\epsilon_j \nu_j(\epsilon_j + U)$$

$$\times \nu_{j'}(\epsilon_j + U) |t_{jj'}|^2 [\langle n_{j'\sigma} n_{j'-\sigma} (1-n_{j\sigma}) n_{j-\sigma} \rangle - \langle n_{j\sigma} n_{j-\sigma}$$

$$\times (1-n_{j'\sigma}) n_{j'-\sigma} \rangle] = W_{j\sigma}(\epsilon_j) + W_{j\sigma}(\epsilon_j + U) \qquad (2)$$

$$\frac{\partial \langle n_{j\sigma} n_{j-\sigma} \rangle}{\partial t} = \sum_\sigma W_{j\sigma}(\epsilon_j + U), \qquad (2a)$$

where $f_{k\sigma}$ is a Fermi distribution function of the electrons in the tip, and $\nu_j(\epsilon_j)$ and $\nu_{j'}(\epsilon_j)$ are the densities of electron states at sites j and j'. Since $U \gg T, |eV_s|$, we have $f_{k\sigma}(\epsilon_j + U) = f_t(\epsilon_j + U) = 0$. In addition, double occupation of a given site is forbid-

den:

$$\langle n_{j\sigma} n_{j-\sigma} \rangle = 0.$$

From Eq. (2a) we find some additional restrictions on the expectation values of the products of the occupation numbers of neighboring sites. Taking those restrictions into account, and summing over σ, we find from Eq. (2) an equation for

$$\langle n_j \rangle = \langle n_{j\sigma} \rangle + \langle n_{j-\sigma} \rangle$$

$$\frac{\partial}{\partial t} \langle n_j \rangle = -\delta_{ij} \Gamma_t (f_t(\epsilon_i) + 1)(\langle n_j \rangle - n_0) + \Gamma_s \sum_{\langle jj' \rangle} \langle n_{j'} \rangle - \langle n_j \rangle, \tag{3}$$

where $\Gamma_t = V_{ki}^2 \nu_t(\epsilon_i)$, $\nu_t(\epsilon_i)$ is the density of electron states in the tip,

$$n_0 = \frac{2f_t(\epsilon_i)}{f_t(\epsilon_i) + 1}; \qquad \Gamma_s = |t_{jj'}|^2 \frac{\Omega_{ph}}{(\epsilon_j - \epsilon_{j'})^2 + \Omega_{ph}^2},$$

Γ_s^{-1} is the time scale of site-to-site transitions, and Ω_{ph} is the uniform broadening of the energy levels due to the intrasite interaction with the phonons or "phase noise."[7] The initial conditions are uniform: $n_j(0) = n_1$. The tunneling current is then given by

$$\langle I(t) \rangle = -e \sum_{k,\sigma} \dot{n}_{k\sigma} = e\Gamma_t (f_t(\epsilon_i) + 1)(\langle n_j(t) \rangle - n_0). \tag{4}$$

A steady-state solution of Eq. (3) is $\langle n_j \rangle = n_0$, $\langle I_{st} \rangle = 0$.

To determine the time dependence $\langle I(t) \rangle$, we take the continuous limit of Eq. (3) for the electron density $n(r,t)$. This continuous limit is a two-dimensional diffusion equation with a sink of unit radius, from which we can find $n(r,t)$ by Laplace transforms. Taking into account the explicit expression for $n(r,t)$ at $\Gamma_{St} \gg 1$, we find the following expression for $\langle I(t) \rangle$:

$$\langle I(t) \rangle \sim \frac{4\Gamma_s e(n_1 - n_0)}{\ln(4\Gamma_s t) + \mu(B)} \tag{5}$$

where

$$B = \Gamma_t (f_t(\epsilon_i) + 1)\Gamma_s^{-1},$$

and

$$\mu(B) \sim 1 \qquad \text{for } B \gg 1$$

$$\mu(B) \sim 2I_0(\sqrt{B})(I_1(\sqrt{B})\sqrt{B})^{-1}, \qquad \text{for } B \sim 1,$$

$$\mu(B) = 4B^{-1} \qquad \text{for } B \ll 1.$$

Actually, $I(t)$ is a random Poisson process. For a tunnel microjunction, the random quantity $\overline{I(t)}^{\tau} = \int_t^{t+\tau} dt' I(t')$ is measured experimentally, where τ is the measurement time. It follows from (5) that under the condition $\tau \ll t$ we have $\langle \overline{I(t)}^{\tau} \rangle = \langle I(t) \rangle + o(\tau/t)$. For the relative current fluctuations we can write

$$\frac{\langle(\overline{I^{\tau}(t)}-\langle\overline{I(t^{\tau})}\rangle)^2\rangle}{\langle\overline{I^{\tau}(t)}\rangle^2}=\frac{e}{\tau\langle\overline{I^{\tau}(t)}\rangle}. \tag{6}$$

Under the condition $e\langle I(t)\rangle^{-1}\ll\tau\ll t$, the relative fluctuations are therefore small, and the measured current $\overline{I^{\tau}(t)}$ is close to $\langle I(t)\rangle$ in the sense indicated.

Depending on the concentration and positions of the adatoms, either the case $B\gg 1$ for the case $B\ll 1$ may be realized experimentally. The current measurement time is usually $\tau\gtrsim 10^{-6}$ s, so that under the condition $B\gtrsim 1$ it would be possible to experimentally observe the behavior in (5) and to estimate Γ_s over times from 10^{-4}–10^{-5} s to a few seconds. After a long time, the relative current fluctuations may be important. If there is a rapid relaxation, $B\ll 1$, the expectation value of the tunneling current is essentially constant at $t\ll\Gamma_s^{-1}\exp[4/B]$: $\langle I(t)\rangle\sim\langle I(0)\rangle$ up to times on the order of several seconds. In contrast with the case $B\gtrsim 1$, under the condition $B\ll 1$ there is the possibility of a tunneling spectroscopy of surface states in a dc regime, although the steady-state value of the current is zero.

Along with surface diffusion, one could study the relaxation associated with transitions to bulk bands, with a time scale γ^{-1}, where $\gamma\ll\Gamma_s$, Γ_t. Under the condition $t\lesssim\gamma^{-1}$, there is essentially no change in the behavior $\langle I(t)\rangle$. If γ is nonzero, then we have $\langle I_{st}\rangle/\langle I(0)\rangle=\gamma/\{\Gamma_t[f_t(\epsilon_i)+1]+\gamma\}$. At these values of γ and Γ_t, however, we would have $\langle I_{st}\rangle/\langle I(0)\rangle\sim 10^{-6}$. In other words, the steady-state current would be negligible.

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[1)] By analogy with the approximation used for the microscopic Hamiltonian in the Anderson model and in the Hubbard model, for strongly localized surface states one can ignore the long-range interactions W_{ij} in comparison with U, the Coulomb repulsion of the electrons with opposite spins which are localized at a common site, by virtue of the relation $U\gg W_{ij}$, where $U\sim e^2/a_i$ and $W_{ij}\sim e^2/eR_{ij}$, where a_i is the radius of the wave function of the localized state, and R_{ij} is the distance between sites.

[2)] Under the conditions $e_j<E_F$ and $V_s>0$, the results also hold for holes.

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