Pis'ma v ZhETF, vol.68, iss.4, pp.299 - 304 © 1998 August 25

THE EFFECTS OF NON-EQUILIBRIUM CHARGE DISTRIBUTION IN SCANNING TUNNELING SPECTROSCOPY OF SEMICONDUCTORS

P.I.Arseyev, N.S.Maslova[+], *S.V.Savinov*[+]

Lebedev Physical Institute RAS, 117924 Moscow, Russia

[+]*Department of Physics, Moscow State University, 119899 Moscow, Russia*

Submitted 3 June 1998
Resubmitted 8 July 1998

Results are presented from a low-temperature scanning tunneling microscopy (STM) investigation of III–V semiconductor surfaces cleaved *in situ* along a (110) plane. The STM topographic images reveal the presence of surface charge structures. The possibility of their observation depends on the charge state of the apex of the STM tip. Peaks are also observed in the local tunneling conductivity spectra. The energy position of these peaks and the energy position of the edges of the band gap change with distance from the defect. A theoretical model is proposed which demonstrates that the experimental scanning tunneling spectroscopy (STS) data can be explained by effects due to a nonequilibrium electron distribution in the contact area, which gives rise to localized charges. In this model the on-site Coulomb repulsion of localized charges and their interaction with semiconductor electrons are treated self-consistently.

PACS: 07.79.-v, 61.16.-d

For a clear understanding of the experimental results, the STM topographic images of surface defects at different values of the tunneling bias voltage must be compared directly with the local spectroscopy data [1]. We present the results of low-temperature STM/STS investigations of atomic defects on the GaAs (110) surface at 4.2 K. The experimental procedure is described in [2]. We have used GaAs single crystals heavily doped with Te ($n = 5 \cdot 10^{17}\,\mathrm{cm}^{-3}$). The typical STM topography of an atomic defect is depicted in the inset in Fig.1. According to the common view [3] this type of defect is a dopant atom residing on the surface.

Normalized conductivity curves measured by means of current-imaging tunneling spectroscopy (CITS) around this kind of atomic defect are presented in Fig.1. Let us mention the main features of the tunneling conductivity curves. The measured band gap edges are shifted by approximately 200 meV near the defect as compared to the flat surface region. A set of peaks around the defect, which are absent above the flat surface, exists in the voltage range from -1 V to 0 V. There is a peak of the tunneling conductivity in the bias range from -1.5 V to -1 V. The position and height of this peak depend on the distance from the defect; this peak does not disappear above the flat surface region.

We assume that the tunneling conductivity peaks in the band gap can be attributed to the Coulomb interaction of the electrons of the sample and induced charges localized both on the STM tip apex and near the defect. We suppose that in this situation the on-site Coulomb repulsion of localized electrons (Hubbard repulsion) is also very important. Such an interaction can change the energy values considerably even for deep impurity levels. As a result, there is a strong dependence of the level energy on the tunneling bias voltage. The experimentally measured position of the peak of the tunneling conductivity

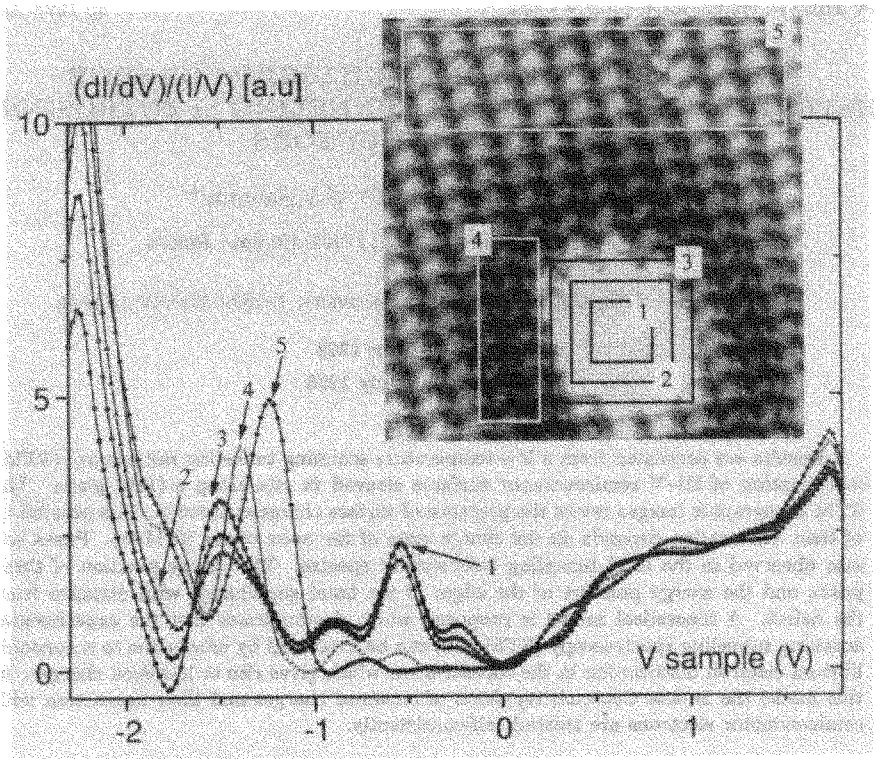

Fig.1. Tunneling conductivity spectra measured near a tellurium atom residing on the cleaved *in situ* (110) GaAs surface at a temperature of 4.2 K. The inset shows the STM image of the 5.8 nm × 5.8 nm surface area from which the spectroscopic data were acquired. Each tunneling conductivity curve is the result of averaging and subsequent numerical differentiation over the surface area which is marked by numbers on the STM topogram

does not coincide with the bulk value of the unperturbed energy levels of the doping impurity.

We have proposed a self-consistent theory for tunneling processes in an STM junction in the presence of impurity states. Various experimental situations can be considered in the framework of this theory. The impurity level can be associated with a surface defect or with a defect in an intermediate layer. The impurity level can also be connected with several atoms or even a single atom on the apex of the STM tip. The proposed theoretical approach includes the following main points. At low temperature and small contact size the steady-state electron distribution is not the thermal equilibrium distribution because of the finite relaxation rate of tunneling electrons [5]. STM/STS measurements can be strongly influenced by a nonuniform charge distribution and the corresponding additional Coulomb interaction [1, 2]. In general, in low-dimensional systems considerable modification of the initial electron spectrum occurs due to the tunneling process itself [4], and charge effects could become very important.

To describe the tunneling processes in an STM junction in the presence of a localized state we use a model which includes three subsystems: an ideal semiconductor, a localized electronic level-surface impurity or tip apex state, and a normal metal (STM tip). These subsystems are coupled by tunneling matrix elements. We add an interaction of the semiconductor with a heat bath in order to describe finite-relaxation-rate effects. The Hamiltonian $\hat{H}$ of the model is thus

$$\hat{H} = \hat{H}_{sc} + \hat{H}_d + \hat{H}_m + \hat{H}_{tun} + \hat{H}_{int} + \hat{H}_{hb}, \quad (1)$$

where $\hat{H}_{sc}$ is the Hamiltonian of the pure semiconductor:

$$\hat{H}_{sc} = \sum_{\mathbf{k},\sigma} (\varepsilon_k - \mu) c^+_{\mathbf{k},\sigma} c_{\mathbf{k},\sigma}, \quad (2)$$

$c_{\mathbf{k},\sigma}$ is the annihilation operator for an electron with momentum $\mathbf{k}$ and spin σ, and μ is the Fermi energy in the semiconductor.

The part $\hat{H}_d$ corresponds to the impurity state and takes into account the Hubbard repulsion:

$$\hat{H}_d = \varepsilon_d \sum_\sigma d^+_\sigma d_\sigma + U/2 \sum_\sigma n^d_\sigma n^d_{-\sigma}, \quad (3)$$

where $n^d_\sigma = d^+_\sigma d_\sigma$, the operator d_σ annihilates an impurity electron with spin σ, and ε_d is the impurity energy level (which in the general case is dependent on the bias V). The part $\hat{H}_{int}$ describes the tunneling between the semiconductor and the impurity state:

$$\hat{H}_{int} = T \sum_{\mathbf{k},\sigma} (c^+_{\mathbf{k},\sigma} d_\sigma + \text{h.c.}), \quad (4)$$

with an interaction matrix element T.

The Hamiltonian of the metal tip $\hat{H}_m$ is

$$\hat{H}_m = \sum_{\mathbf{p},\sigma} (\varepsilon_p - \mu - eV) a^+_{\mathbf{p},\sigma} a_{\mathbf{p},\sigma}, \quad (5)$$

where $a_{\mathbf{p},\sigma}$ is the annihilation operator for a tip electron with momentum $\mathbf{p}$ and spin σ, and V is the applied bias voltage.

The part $\hat{H}_{tun}$ corresponds to the impurity–metal-tip hopping (tunneling) term with matrix element T':

$$\hat{H}_{tun} = T' \sum_{\mathbf{p},\sigma} (a^+_{\mathbf{p},\sigma} d_\sigma + \text{h.c.}). \quad (6)$$

Finally, $\hat{H}_{hb}$ describes the interaction of the semiconductor electrons with a heat bath, which leads to a finite relaxation time of nonequilibrium electrons. The kind of heat bath is not crucial for our purposes and we choose the simplest form:

$$\hat{H}_{hb} = \sum_{\mathbf{k},\mathbf{p}',\sigma} T''(\mathbf{k} - \mathbf{p}') (c^+_{\mathbf{k},\sigma} b_{\mathbf{p}',\sigma} + \text{h.c.}) \quad (7)$$

where $b_{\mathbf{p}',\sigma}$ is the annihilation operator for a heat bath electron with momentum $\mathbf{p}'$ and spin σ, and $T''(r)$ is the effective interaction with the heat bath.

As we have said, an additional charge associated with localized states in the contact area can appear if the finite relaxation rate is taken into account. The influence of this charge on the tunneling characteristics can be considered self-consistently in the following way [6].

a) The Coulomb interaction of the Hubbard type is treated self-consistently in the mean-field approximation. The characteristic scales of the STM junction and the possible radius of a localized state on the apex of the tip have values $a_0 \simeq 5$–10 Å. Thus the

Coulomb repulsion $U = e^2/a_0$ should have a value of the order of the semiconductor band gap (0.5–1.0 eV), which is much smaller than bandwidths of the semiconductor and the metallic tip. Thus we suppose that the constraint on double occupancy (of a localized state) is not essential for our problem. It is well known that Coulomb correlations in Hubbard-type systems begin to play a significant role only if U is greater than the bandwidth. For smaller U the mean-field approximation gives satisfactory results. Thus the Coulomb interaction leads to a dependence of the localized state energy on the additional charge density: $\varepsilon_d = \varepsilon_d^0 + U\delta n_d$, where U presumed to lie in the region 0.5–1 eV.

b) A potential W is introduced to describe the interaction of semiconductor electrons with the additional charge δn_d present on the localized state. The corresponding interaction Hamiltonian has the form

$$\hat{H}_W = \sum_{\mathbf{k},\mathbf{k}'} W(\mathbf{k}-\mathbf{k}')c^+_{\mathbf{k},\sigma}c_{\mathbf{k}',\sigma}. \tag{8}$$

Exact calculation of the electrostatic potential W is possible only if the exact geometry of the contact is known. Usually the details of the shape of the tip apex and, consequently, the spatial distribution of the electric field cannot be determined. Nevertheless, there are two possible cases for which the analysis can be simplified. If the charge screening in the semiconductor is weak, the effective radius R of the potential is much greater than the interatomic distance $R \gg a$. Then $W(\mathbf{k}-\mathbf{k}') = w \times \delta n_d \delta_{k,k'}$, with the parameter w determined by the particular contact configuration. The potential is almost constant at distances greater than the contact area. This case is similar to band-bending effects in planar tunnel junctions in the presence of an applied bias. In such a situation one can observe a shift of the gap edges in tunneling experiments [7]. The other case is encountered if the geometry of the contact or strong screening in the semiconductor leads to a point-like effective potential — the effective radius R of the potential is of the order of the interatomic distance a. Then $W(\mathbf{k}-\mathbf{k}') = w \times \delta n_d$. In this case we are interested in the point-like potential caused by the localized charge both on the apex of the STM tip and on semiconductor surface defects. For charge localized on the tip the constant w is determined by the distance from the tip to the semiconductor surface. Typical values of the tip–sample separation d in STM junctions do not exceed 10–15 Å. Thus the simplest estimate of the Coulomb potential (e^2/d) at the semiconductor surface yields $w \simeq 0.3$–0.5 eV. In any case Coulomb effects should be taken into account, because the tip–sample separation and typical radius of a localized state are comparable to the interatomic distance. The extra charge on a localized state and the tunneling conductivity of a system can be determined by means of a self-consistent approach based on a diagram technique for nonequilibrium processes [7].

The tunneling conductivity $dI/dV(\omega)$ can be determined from the corresponding kinetic equations for Keldysh Green functions in terms of nonequilibrium occupation numbers $n_d(\omega)$ of the localized state:

$$dI/dV(\omega) \quad = \quad -4\gamma_0 \mathrm{Im} G^R_{d,d}(\omega)(n_d(\omega) - n_d^0(\omega)) \tag{9}$$

where $n_d^0(\omega)$ is the equilibrium occupation number of the localized state, and $G^{R(A)}_{d,d}(\omega)$ is the exact retarded (advanced) Green function of the localized state.

The sample and contact characteristics appear in the final expression for the tunneling conductivity as relaxation and kinetic constants (functions):

$$-i\gamma_0(\omega) = -i|T'|^2\nu_{\mathbf{p}}(\omega) \qquad -i\gamma(\omega) = -i|T''|^2\nu_{\mathbf{p}'}(\omega)$$

$$\Gamma_d = -\gamma_0 \mathrm{Im} G^R_{dd} \qquad \Gamma_k = -\gamma \sum_{\mathbf{k},\mathbf{k}'} \mathrm{Im} G^R_{\mathbf{k},\mathbf{k}'} \qquad \Gamma = T^2 \nu_k \tag{10}$$

where ν_k is the conduction-band density of states, and $\nu_{\mathbf{p}}(\omega)$ and $\nu_{\mathbf{p}'}(\omega)$ are, respectively, the densities of states in the metallic tip and in the heat bath connected to the semiconductor.

The final expression for the tunneling conductivity after all substitutions can be written as

$$\begin{aligned} dI/dV(\omega) &= \frac{2\Gamma_d\Gamma_k(\Gamma/T)(Z_2+Z_2^0)}{\Gamma_d\Gamma_k+\Gamma_k(\Gamma/T)Z_2+\Gamma_d(\Gamma/T)(Z_1^0+Z_2^0+Z_2)} \\ &\times \left(n_p^0(\omega)-n_k^0(\omega-eV)\right), \end{aligned} \tag{11}$$

where $n_p^0(\omega)$ and $n_k^0(\omega-eV)$ are the equilibrium occupation numbers of the states of the semiconductor and metallic tip, respectively. The dimensionless functions Z are given by

$$\begin{aligned} Z_1^0 &= 2\frac{\gamma}{T}\mathrm{Im}\left[\left(G_d^A(\omega)(\omega-\tilde{\varepsilon}_d)-1\right)\alpha(\tilde{\varepsilon}_d)\right] \\ Z_2 &= 2T\mathrm{Im}\, G_d^R(\omega)\mathrm{Im}(\alpha(\tilde{\varepsilon}_d)) \\ Z_2^0 &= 2\gamma_0 T\mathrm{Im}\left[\left(G_d^R(\omega)\left(1-i\gamma\frac{\omega-\varepsilon_d+i\gamma_0}{T^2}\right)+i\frac{\gamma}{T^2}\right)\frac{\alpha(\tilde{\varepsilon}_d)-\alpha(\omega)}{\omega-\tilde{\varepsilon}_d}\right] \\ \alpha(\omega) &= \nu_k^{-1}\sum_{\mathbf{k}}\frac{1}{\omega-\varepsilon_{\mathbf{k}}+i\delta} \end{aligned} \tag{12}$$

where $\tilde{\varepsilon_d} = \varepsilon_d + i\gamma_0$.

The additional charge δn_d is determined self-consistently from the exact nonequilibrium occupation numbers and the density of states on the localized state. Both these parameters are functions of the applied bias voltage and the value of the additional charge, since they depend on $\varepsilon_d = \varepsilon_d^0 + U\delta n_d$ and the Coulomb potential $W(\delta n_d)$ (Eq.8):

$$\begin{aligned} \delta n_d(V) &= \int[(-1/\pi)\mathrm{Im}G^R_{d,d}(\omega,V)n_d(\omega,V) - \\ &- (-1/\pi)\mathrm{Im}G^R_{d,d}(\omega,V=0)n_d^0(\omega,V=0)] \end{aligned} \tag{13}$$

The analytical expression for the dependence of the tunneling conductivity on the applied voltage for the two situations described was analyzed numerically. The results for typical parameter values (relaxation rates γ and γ_0, tunneling rate Γ, and initial impurity level ε_d^0) are depicted in Fig.2. Two different situations were investigated: 1) ε_d^0 lies in the band gap (Fig.2, curves *1–3*); 2) there is one or a few localized states in the conduction or valence band (Fig.2, curves *4,5*). We present in Fig.2 the results of calculations for the Coulomb parameters $U = 1\,\mathrm{eV}$ and $w = 0.5\,\mathrm{eV}$. The qualitative behavioral features of the tunneling conductivity are insensitive to some variations of the Coulomb parameters within the regions estimated above. The initial model density of states for the semiconductor is shown by the dotted curve. It obviously differs from the tunneling conductivity curves that could be obtained in STS measurements. One can clearly see the shift of the gap edges, which becomes more pronounced with decreasing relaxation rates (Fig.2, curves *4,5*). A nonequilibrium electron distribution leads to charge accumulation on a localized state, with initial energy ε_d^0. Because of Coulomb repulsion this results in a simultaneous change of its energy by an amount $\Delta\varepsilon$ which is comparable

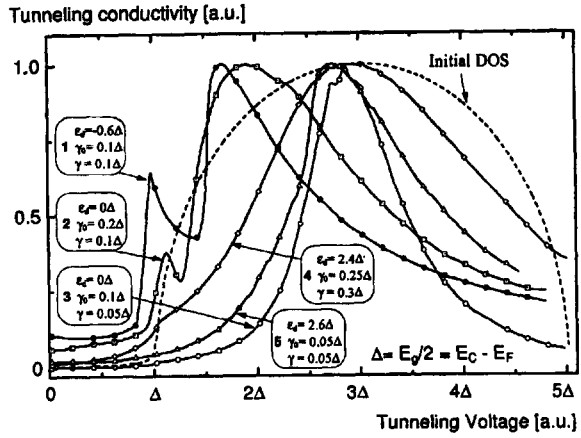

Fig.2. Tunneling conductivity curves obtained numerically from Eq.(11) for different values of the STM junction parameters: the relaxation rate in the semiconductor γ, the relaxation rate on the localized state γ_0, and initial localized state energy ε_d^0. All quantities are measured in units of one-half the initial band-gap width Δ. The values of Coulomb parameters are: $U = 2\Delta, w = \Delta$. The unperturbed initial model density of states is shown by the dotted curve

to the value of the band gap. In this situation a localized state is often manifested as a peak occurring near the band edge (Fig.2 curves *1,2*) regardless of its initial energy. Near the band edge the tunneling current grows rapidly with tunneling bias, thus strongly changing the localized charge. Such a peak can appear above the flat surface area if the localized state is associated with the apex of the STM tip. This can be seen from curve *1* in Fig.1, which shows the experimental curves of the tunneling conductivity. The peak position is sensitive to variations of the characteristic parameters Γ, γ, γ_0, and ε_d, which determine the value of the additional charge. But the peak is not very sensitive to the position of the Fermi level relative to the band gap edges.

Our model can be generalized for situations in which there are several localized states ε_d^i associated both with the apex of the STM tip and with the defect.

As the charge accumulated in a localized state ε_d is determined by the relaxation and tunneling rates, it depends on the tip–sample and tip–defect separation. By changing the STM tip position one can obtain various tunneling conductivity curves with different peak positions. The shift of the gap edges and the tunneling conductivity peaks that are sensitive to changes in the tip position can be seen in Fig.1. They can be qualitatively understood in terms of the proposed theoretical model.

The work performed in Moscow has been supported by the Russian Ministry of Research (Surface Atomic Structures, Grant 95-1.22; Nanostructures, Grant 97- 1086) and the Russian Foundation for Basic Research (RFBR, Grants 96-02-19640a and 96-02-16701a).

1. N.S.Maslova, V.I.Panov, S.V.Savinov eta al., JETP Lett., **67**, 131 (1998)
2. N.S.Maslova, V.I.Panov, S.V.Savinov et al., Phys. Low Dim. Struct, to be published
3. J.F.Zheng, X.Liu, N.Neuman et al., Phys. Rev. Lett. **72**, 10, 1490 (1994).
4. P.I.Arseev and N.S.Maslova, Sov. JETP **102**, 1056 (1992).
5. O.Agam, N.S.Wingreen, and B.L.Altshuler, Phys. Rev. Lett. **78**, 1956 (1997).
6. P.I.Arseev, N.S.Maslova, V.I.Panov, and S.V.Savinov, *Role of charge effects in tunneling investigations of semiconductors*, Semiconductors-97, December 1-5, Moscow, 1997.
7. R.M.Feenstra and J.A.Stroscio, J. Vac. Sci. Technol.**B5**, 923 (1987).
8. L.V.Keldysh, Sov. Phys JETP **20**, 1018 (1964).

Edited by Steve Torstveit