Novel Transport Effects in High-Bias Ballistic-Electron-Emission Spectroscopy

R. Ludeke

IBM T.J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598

(Received 26 June 1992)

Pronounced structure at large biases in the ballistic-electron-emission-microscopy current for Cr/GaP(110) is attributed to density-of-states effects in GaP. Quasielastic scattering at the Cr-GaP interface appears vital for the effect. Impact ionization in the GaP is invoked to explain the unusually large collector currents that can exceed the injected STM tip current.

PACS numbers: 73.40.Gk, 71.20.−b, 72.20.Ht, 73.50.Fq

Ballistic-electron-emission microscopy (BEEM), a scanning tunneling microscope (STM) based microscopy and spectroscopy, has been used in the past as a threshold technique to measure potential steps, in particular Schottky barriers, at semiconductor interfaces [1–5]. As such, it has given Schottky barrier heights ϕ_{SB} of unprecedented precision and repeatability [5,6]. Reported measurements have been restricted in general to tip biases $V_T \lesssim 2.5$ V due, in part, to inherent current instabilities at higher biases [7]. In addition, the collector or BEEM current I_c exhibited no obvious structure, although weak structure in the derivative spectra has been assigned to current injection into higher-lying band extrema [2,3], as well as to band-gap excitations and phonon effects in the semiconductor [8]. The use of Cr films minimizes current instability problems and we report here BEEM spectra for Cr on GaP at tip biases up to 10 V. More importantly, we observed pronounced structure above 3 V, which we attribute to final-state effects in the semiconductor, specifically to transport processes constrained by the bulk conduction band density of states (DOS) of the GaP. The results thus represent, to the best of our knowledge, the first direct observation of bulk DOS effects in transport measurements [9]. Furthermore, the observed current response at high biases represents a transport regime outside the conventional view of BEEM transport, in that scattering, particularly at the interface, and the ensuing directional randomization of the electrons, are essential parts of the process that leads to the observed spectral response.

The samples consisted of 30–70-Å-thick Cr dots, 1 or 2 mm in diameter, deposited in ultrahigh vacuum (UHV) on *in situ* cleaved (110) surfaces of *n*-type GaP (Te doped to $\sim 10^{18}$ cm^{-3}). After sample transfer into the STM, the Cr dot was gently contacted with an Au wire held at ground potential. Further details of the UHV instrument can be found elsewhere [10]. The surface morphology of the Cr films, as deduced from the STM images, consists of a granular structure composed of faceted nodules 10–20 Å in height by 50–100 Å in diameter and comprising about 25% of the surface area. These clusters are dispersed over an undulating background covered with finer, sometimes elongated, features 2–5 Å in height and 20–50 Å in lateral extent. Collector current is detected mainly in the valleys between the larger clusters and, particularly, on the smoother sections of the sample surface. The net area where the film is relatively flat and parallel to the interface—a condition necessary to detect a quantifiable collector current [5,6]—constitutes ~10% of the total area. However, these areas are readily identified by using the BEEM imaging model [1]. The I_c vs V_T curves were measured in the conventional constant-current mode, with STM tip currents (I_T) in the range of 1–5 nA. Usually an array of sixteen spectra was taken in one scan sequence; the scan sequences were repeated at different locations of the sample, as well as on different samples. Representative spectra are shown in Fig. 1(a). The bias corresponds to electron injection into the Cr, and hence represents injection into empty states.

Striking features in the spectra of Fig. 1(a) include the pronounced double-hump structure, the large I_c for curve (i) that exceeds I_T for $V_T \gtrsim 7.5$ V, and the excellent signal-to-noise ratio over most of the bias range. Present models for current transport [2,6], which are based on parabolic, free-electron-like bands—and hence are expected to be valid only over a narrow (~0.5 V) range

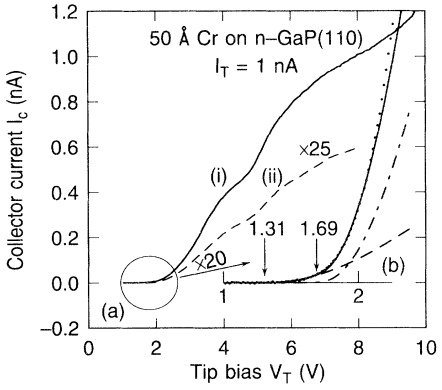

FIG. 1. (a) Single scans of I_c for Cr/GaP(110): curve (i), on locally smooth section of surface; curve (ii), on a rougher protruding section (shown magnified ×20). (b) Expanded and magnified (×20) threshold region of curve (i): dots represent the experimental data; solid line is a fit with two current components with thresholds at 1.31 V (dashed curve) and 1.69 V (dashed-dotted curve).

of parabolicity for a single band—cannot explain the observed spectra. Even with the inclusion of electron scattering in the Cr layer and/or additional transmission channels for transport across the interface at higher thresholds, a satisfactory fit was obtained only for $V_T \lesssim 2$ V, which is consistent with our previous fits [6]. An expanded view of the spectrum (i) for $1 \leq V_T \leq 2.4$ V is shown in Fig. 1(b). A proper fit to the current with present "threshold" models can only be made over this portion of the spectrum. Here, such a fit consists of the sum of two components with different thresholds; the lower one corresponds to the usual ϕ_{SB} for electron transfer into the lowest conduction band minima near X_1, and the second to transfer into the higher-lying L_1 and X_3 critical points. Using a previously described $\frac{5}{2}$ power law that includes inelastic scattering in the metal [5,6], threshold voltages of 1.31 ± 0.02 V and 1.69 ± 0.02 V were obtained from the computer-aided fits. The difference between the thresholds of 0.38 ± 0.02 V corresponds to an average of the X_1-X_3 and X_1-L_1 separations of the conduction band critical points at room temperature; for comparison, differences deduced from optical data taken at 80 K are 0.28 eV and 0.53 eV, respectively [11]. A second threshold was not required in previous fits over a narrower bias range for GaP [5,6]. This region of the spectrum is the truly ballistic regime, in which a large fraction of electrons injected by the tunneling tip traverse the metal film without scattering and a fraction of these are collected in the semiconductor, as shown schematically in Fig. 2(a).

Unusually intense I_c's, such as curve (i) in Fig. 1 were observed on the smoother depressions of two samples with

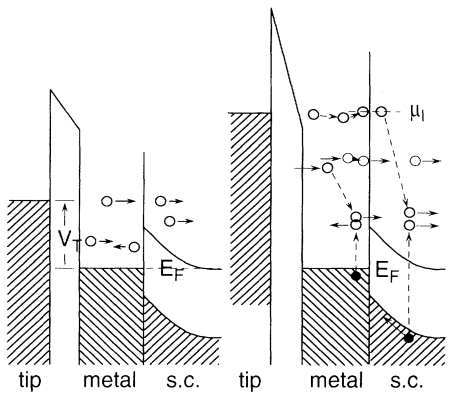

FIG. 2. (a) Conventional BEEM picture representing the coherent limit. (b) For high-bias conditions scattering dominates in the metal; impact ionization (represented by vertical events) depicts electron multiplication in both metal and semiconductor. Black circles represent holes. The broad energy distribution of electrons in the metal raises the quasi Fermi energy level to μ.

average thicknesses of 30 and 50 Å. Other rougher regions of the surface yielded curves of the same shape, but of intensities reduced by up to 2 orders of magnitude, an example of which is shown in Fig. 1(a), curve (ii). Whenever observed, the curves exhibited identical spectral features and were totally reproducible for a given location on the surface. On the prevailing regions with high surface gradients, and particularly on top of the larger protrusions, little ($\lesssim 1$ pA) or no current could be observed. The large I_c's are attributed to both an effective tip injection geometry at locally thin and smooth portions of the Cr layer that are parallel to the interface, as well as to efficient electron scattering at the interface and impact ionization in the semiconductor. Electron-electron scattering in the metal layer [12] can account for some electron multiplication via impact ionization [13], but the effectiveness of this mechanism requires that the film is thin enough to allow the secondaries to reach the interface (their energy distribution is peaked around $eV_T/2$, which gives them an enhanced mean free path, albeit with a broader angular distribution), but thick enough so as not to suppress electron-electron scattering entirely. In the semiconductor, hot electrons with kinetic energy $E_{KE} \gg E_g$, the band gap energy, deenergize or cool as well through impact ionization by creating electron-hole pairs that separate in the depletion region (~ 400 Å for the GaP used here), as schematically shown in Fig. 2(b). Impact ionization is an effective electron multiplication scheme exploited in avalanche photodiodes [14], and believed to be responsible for the large I_c observed here. In contrast, free carrier and phonon scattering, which dominate at $E_{KE} < E_g$ (2.3 eV) tend to reduce the current. For $Al_{0.9}Ga_{0.1}As$, a comparable material with $E_g = 2.13$ eV, impact ionization was reported to dominate for $E_{KE} > 4.5$ eV [15].

However, inelastic scattering in the metal and impact ionization in the GaP should not produce structure other than current increases (thresholds) near tip biases of 2.6 V ($2\phi_{SB}/e$) for the former and near 3.6 V [$(E_g + \phi_{SB})/e$] for the latter. Such thresholds are not observed in our spectra. Nevertheless, inelastic scattering in the metal is expected to contribute a smooth and structureless background to I_c of an intensity that depends on the generation of secondaries and their ability to overcome the barrier. However, in view of both the weak I_c for ballistic injection near threshold, and the broad angular distribution of secondaries, which far exceeds the acceptance cone near threshold [2], one would not expect a strong increase in I_c from secondaries with energy exceeding ϕ_{SB}. Stated differently, the semiconductor phase space available for secondaries of $E_{KE} \sim \phi_{SB}$ is small compared to that available to electrons of twice that energy that were not inelastically scattered. The similarities of spectral features in curves (i) and (ii) of Fig. 1, which only differ in intensity that is directly attributable to enhanced inelastic scattering in the metal for curve (ii), corroborates

the notion that the observed structure is not due to scattering in the Cr. Similarly, the energy dependence of the scattering rate and quantum yield for impact ionization in Si, and presumably other semiconductors, exhibits a very soft threshold above the gap energy [15], reveals little structure, and is largely insensitive to band structure details [16]. Consequently, structure in I_c cannot be attributed directly to inelastic scattering in either metal or semiconductor. The possibility of structure in I_c arising from coherent interference effects in the tunnel gap or in the metal film were considered as well, but deemed unlikely. The constant-current mode of injection suppresses any variation of the tunnel current due to barrier resonances. On the other hand, the strong scattering in the metal, as well as the demonstrated insensitivity of the spectra to thickness variations precludes coherent interference effects in the metal film.

To identify the source of structure we must look at the transport process near the interface, as well as across it, in more detail. Another important ingredient in this process is quasielastic scattering by impurities and phonons in the metal film, which in bulk exhibits a mean free path that increases with energy [13]. In the present case, the mean free path is expected to exceed the Cr film thickness [13], so that most quasielastic scattering occurs near the interface. Because of the reactivity of Cr [17], the Cr-GaP interface will be disordered on a microscopic scale, as well as contain impurities due to limited alloying and interdiffusion. The mere crystallographic mismatch between Cr and GaP, as well as the disorder, defects, and roughness at the interface contribute strongly to quasielastic scattering, a process that effectively invalidates the tenet of transverse momentum conservation, which was tacitly assumed in previous BEEM transport modeling [2,4,6,18]. Thus the Cr film, and particularly its interface, can be looked at as a source of crystal momenta that provides the transmitted electrons accessibility to semiconductor phase space restricted essentially only by energy conservation. The consequences of scattering render the previous closed-form approaches unsuitable; instead calculation of I_c must consider four quasi-independent steps: (i) tip injection, (ii) electron diffusion through the Cr film to the interface, (iii) transport across the interface, and (iv) hot electron transport in the semiconductor, as shown schematically in Fig. 2(b). Since the tip current is held constant, and transport through the metal and semiconductor do not contribute to structure, we conclude that the latter derives mainly from constraints imposed by transport across the interface.

Transport across metal-oxide-metal and metal-semiconductor interfaces has been extensively reported in the tunneling literature of the 1960's and '70's [19]. Regardless of the approach, the tunneling current is an integral over all allowed energies involving the DOS of the electrodes. A convenient formalism for the present case is the zero-barrier-width approach in the strong coupling limit developed by Feuchtwang [20]. His expression [Eq. (4.4)] for the current density is

$$J_c = \frac{4\pi e}{\hbar^2}\int_{-\infty}^{\infty} |\Lambda(E)|^2 [f_m(E) - f_{sc}(E)]\rho_m(E)\rho_{sc}(E)dE \,, \tag{1a}$$

which in the low-temperature limit becomes

$$J_c = \frac{4\pi e}{\hbar^2}\int_{E_F}^{E_F+\mu_1} |\Lambda(E)|^2 \rho_m(E)\rho_{sc}(E)dE \,, \tag{1b}$$

where $|\Lambda(E)|^2$ is a matrix element, $f(E)$ the Fermi function, and $\rho(E)$ the density of states in the metal (m) and semiconductor (sc). $\mu_1 \approx eV_T$ is the change in the upper limit of the occupied states in the metal at the interface due to the modified electron distribution resulting from injection and scattering, as shown schematically in Fig. 2(b). Differentiating Eq. (1b) with respect to V_T gives

$$dJ_c/dV_T \approx (4\pi e^2/\hbar^2)|\Lambda(E)|^2 \rho_m(E)\rho_{sc}(E) \,. \tag{2}$$

Thus dJ_c/dV_T is proportional to the product of the density of states in the metal and the semiconductor, as well as the matrix element. The latter is generally assumed to be only weakly dependent on the energy [19,20], and is not expected to contribute to structure in the conductivity. Thus the source of structure derives mainly from the density of states. We will first examine possible structural contributions from ρ_m above E_F. This quantity is proportional to $(dI_T/dV_T)/(I_T/V_T)$. For our Cr film neither dI_T/dV_T nor I_T/V_T indicated any evidence of structure over the entire bias range (not shown). Additional confirmation of a featureless and nearly flat conduction band DOS in the 2–10-eV range comes from both Bremsstrahlung isochromat spectra and calculated DOS for Cr [21], which only show a strong d-electron peak within 2 eV of E_F. Although not an issue here, even the d electrons do not appear to contribute to structure in tunneling experiments, a fact attributed to the rapid decay of d states in the barrier [22]. Consequently, we arrive at the conclusion that the structure in I_c arises mainly from the empty DOS of GaP. To test this notion we plot in Fig. 3

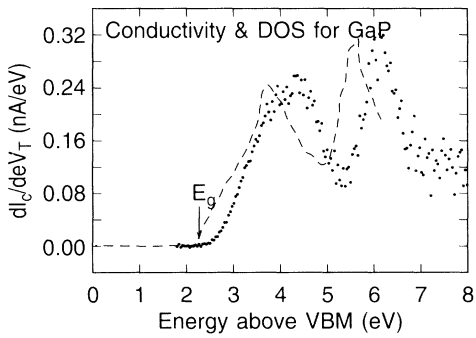

FIG. 3. dI_c/dV_T (dots) compared with empirical pseudopotential DOS (dashed line) from Chelikowsky, Chadi, and Cohen [23].

dI_c/dV_T, for which twelve I_c curves, like (i) in Fig. 1(a), were averaged to improve the statistics. The result should closely resemble the conduction band DOS of GaP. The comparison with a theoretical DOS [23], as experimental data are not available, is shown in Fig. 3 as a dashed line. We have referenced both curves to the top of the valence band, which for the experimental data corresponds to adding 0.96 eV ($E_g - \phi_{SB}$). The ordinate of the DOS was scaled to agree with the experimental data. The agreement is certainly satisfactory in view of the theoretical difficulties of precisely calculating the energies of conduction band states. Nevertheless, both the relative intensities and widths of the two peaks are consistent between theory and experiment.

In summary, we have shown that through the application of large biases BEEM can be a viable tool to determine features of the conduction band DOS of semiconductors, as well as a potential tool for studying hot carrier dynamics in metal-semiconductor systems. This suggests that a new approach must be used to calculate I_c in the limit where scattering near the interface dominates the momentum and energy redistribution of electrons that can transfer into the semiconductor; an approach that must also include impact ionization effects in the semiconductor.

The technical assistance of M. Prikas is gratefully acknowledged. Useful discussions with M. Fischetti and P. Price helped in clarifying aspects of transport issues discussed here.

[1] W. J. Kaiser and L. D. Bell, Phys. Rev. Lett. **60**, 1406 (1988).

[2] L. D. Bell and W. J. Kaiser, Phys. Rev. Lett. **61**, 2368 (1988).

[3] A. E. Fowell, R. H. Williams, B. E. Richardson, and T.-H. Shen, Semicond. Sci. Technol. **5**, 348 (1990); T. H. Shen, M. Elliot, A. E. Fowell, A. Cafolla, B. E. Richardson, D. Westwood, and R. H. Williams, J. Vac. Sci. Technol. B **9**, 2219 (1991).

[4] L. J. Schowalter and E. Y. Lee, Phys. Rev. B **43**, 9308 (1991).

[5] M. Prietsch and R. Ludeke, Phys. Rev. Lett. **66**, 2511 (1991).

[6] R. Ludeke, M. Prietsch, and A. Samsavar, J. Vac. Sci. Technol. B **9**, 2342 (1991).

[7] H. D. Hallen, A. Fernandez, T. Huang, R. A. Buhrman, and J. Silcox, J. Vac. Sci. Technol. B **9**, 585 (1991).

[8] E. Y. Lee and L. J. Schowalter, Phys. Rev. B **45**, 6325 (1992).

[9] Bremsstrahlung isochromat spectroscopy (BIS) is the only other known technique to probe directly the bulk conduction band density of states over a broad energy range. It has been applied to Si, Ge, GaAs, and ZnSe by W. B. Jackson and J. W. Allen, Phys. Rev. B **37**, 4618 (1988).

[10] M. Prietsch, A. Samsavar, and R. Ludeke, Phys. Rev. B **43**, 11 850 (1991).

[11] *Numerical Data and Functional Relationships in Science and Technology*, Landolt-Börnstein, New Series Vol. 17a, edited by O. Madelung, M. Schulz, and H. Weiss (Springer-Verlag, Berlin, 1982), Chap. 2.9. The separation of these two critical points is too small to warrant a fit with separate thresholds.

[12] J. J. Quinn, Phys. Rev. **126**, 1453 (1962). The mean free path for electron-electron scattering $\sigma_{e\text{-}e} \propto [eV + E_F]^{1/2}/(eV)^2$ in the free-electron approximation, which overestimates the reductions in $\sigma_{e\text{-}e}$ with energy (Ref. [13]).

[13] C. R. Crowell and S. M. Sze, in *Physics of Thin Films*, edited by G. Hass and R. F. Thun (Academic, New York, 1967), Vol. 4.

[14] F. Capasso, in *Semiconductors and Semimetals*, edited by R. K. Willardson and A. C. Beer (Academic, Orlando, 1989), Vol. 22D, Chap. 1.

[15] E. A. Eklund, P. D. Kirchner, D. K. Shuh, F. R. McFeely, and E. Cartier, Phys. Rev. Lett. **68**, 831 (1992); E. Cartier, M. V. Fischetti, E. A. Eklund, and F. R. McFeely, unpublished results for Si.

[16] J. Bude, in *Monte Carlo Device Simulation: Full Band and Beyond*, edited by K. Hess (Kluwer Academic, Boston, 1991), Chap. 2.

[17] The Cr/GaP interface chemistry has not been reported, but should be similar to both the reactive Cr/GaAs [B. M. Trafas, D. M. Hill, P. J. Benning, G. D. Waddill, Y. N. Yang, R. L. Siefert, and J. H. Weaver, Phys. Rev. B **43**, 7174 (1991)] and other reactive transition metals on GaP [R. Ludeke, M. Prietsch, A. B. McLean, and A. Santoni, J. Vac. Sci. Technol. B **8**, 964 (1990)].

[18] M. D. Stiles and D. R. Hamann, Phys. Rev. B **40**, 1349 (1989); J. Vac. Sci. Technol. B **9**, 2394 (1991).

[19] For a general review, see E. L. Wolf, *Principles of Electron Tunneling Spectroscopy* (Oxford Univ. Press, New York, 1985).

[20] T. E. Feuchtwang, Phys. Rev. B **10**, 4121 (1974).

[21] W. Speier, J. C. Fuggle, R. Zeller, B. Ackermann, K. Szot, F. U. Hillebrecht, and M. Campagna, Phys. Rev. B **30**, 6921 (1984).

[22] G. I. Rochlin and P. K. Hansma, Phys. Rev. B **2**, 1460 (1970).

[23] J. R. Chelikowsky, D. J. Chadi, and M. L. Cohen, Phys. Rev. B **8**, 2786 (1973).