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Ballistic-hole spectroscopy of interfaces

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A new technique allows direct control and measurement of ballistic-hole transport through interfaces. This spectroscopy has been applied to determine the detailed properties of hole transmission through metal-semiconductor interfaces and probe the valence-band structure of subsurface semiconductor heterostructures. The ballistic-hole probe is created by electron-tunneling-microscopy methods and provides high-spatial-resolution capabilities.

The primary importance of semiconductor interface electronic structure in the understanding of electronic transport and in semiconductor technology inspires intense research activity.[1] For decades the fundamental properties of charge-carrier transport through interfaces have been experimentally investigated by a wide range of techniques. However, a detailed, energy-resolved spectroscopy of electron transport in metals, semiconductors, and through semiconductor interfaces has only recently become available. Ballistic-electron-emission microscopy (BEEM) methods enable direct spectroscopy of subsurface interface electronic structure on a nanometer spatial scale.[2-4] The energy-resolved spectroscopy methods based on BEEM have been limited to investigation of electron transport. The properties of hole transport, however, in semiconductors and metals, through interfaces, and through tunnel barriers is central to the understanding and development of quantum well, superlattice, and other important systems. In addition, a hole spectroscopy is required for the measurement of the crucial interface valence-band offset and valence-band structure at semiconductor interfaces. In this Rapid Communication we report energy-resolved, ballistic-hole spectroscopy of interface transport and interface electronic structure. This new method has enabled direct measurement of subsurface *valence-band* Schottky barrier height and valence-band structure. The experimental spectra reveal the critical properties determining hole transport through interfaces. In addition, a theoretical treatment of ballistic-hole interface spectroscopy is in excellent agreement with the experimental spectra.

Ballistic-hole spectroscopy is enabled by the creation of a nonequilibrium hole distribution. Previously developed BEEM techniques were based on the vacuum tunneling of electrons from a tunneling tip to the interface structure under investigation. As shown in Fig. 1(a), the ballistic-electron distribution created by tunneling is collected after transport through a multilayer structure. In contrast, ballistic-hole spectroscopy, shown in Fig. 1(b), is based on tunneling of electrons from the interface structure to the tunnel tip with tip bias positive with respect to the structure (tunnel bias, V, negative). For negative V, where tunneling probes occupied states in the base, the emission of an electron from the base electrode of the interface structure creates a hole in the conduction band of the base material. Since hole attenuation lengths are as large as several hundred angstroms,[5] the hole may propagate ballistically through the base electrode and to the subsurface interface. Transmission through the interface is allowed if the hole energy (measured with respect to the base conduction-band minimum) is less than the threshold defined by the valence-band maximum ($E_F - eV_b$). Additional conditions on hole transport are described below. Since the ballistic-hole energy is directly determined by the applied bias, an accurate hole spectroscopy of interface transport and interface valence-band structure is now possible. Further, since a wide variety of interface systems may be investigated with this method, fundamental transport properties in many materials may be directly measured in a broad energy range below the Fermi energy. It is particularly important to note that, as for electron-based BEEM, this ballistic-hole spectroscopy of subsurface electronic structure is performed with nanometer spatial resolution, enabling investigation of ideal interface properties as well as defect properties.[2-4]

Ballistic-hole spectroscopy is performed by measuring hole current transmitted through the interface and reaching the collector as a function of tunnel bias, V, applied between tip and base. Since the collector current measured between the collector and base terminal is typically less than 100 pA, a sensitive, low-noise preamplifier system must be employed for current detection. The current amplifier noise decreases with increasing impedance of the base-collector junction. Since junction impedance depends on thermally activated processes,[6] for low energy-barrier interface systems it is necessary to perform BEEM measurements at low temperature to obtain large impedance and low-noise spectra. In addition, reduction in the BEEM system operating temperature results in reduced smearing of the tunnel tip Fermi distribution and, therefore, improved spectral energy resolution. The experimental results reported here were obtained with a BEEM apparatus employing a scanning tunneling microscope system[7] operating immersed in liquid nitrogen. The

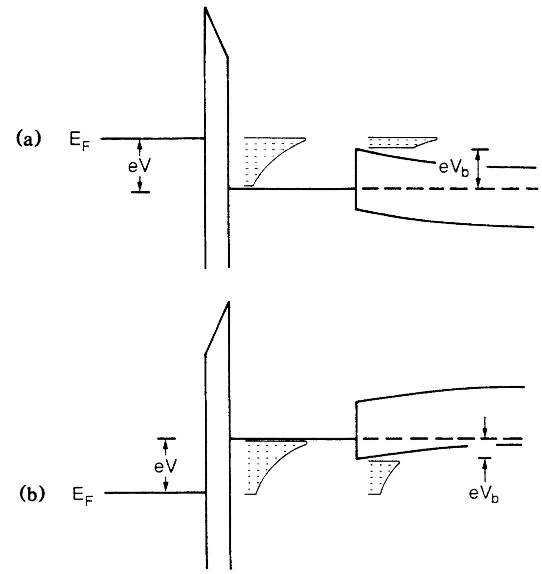

FIG. 1. Comparison of BEEM ballistic-electron and -hole spectroscopies of subsurface interface conduction and valence bands. The tunnel voltage V and the Schottky barriers eV_b between the Fermi levels and the conduction minimum and valence-band maximum are shown. The ballistic-electron and -hole distributions reflecting the tunnel probability distribution are indicated in the metal-base regions and in the semiconductor collectors. (a) Ballistic-electron spectroscopy of a metal-semiconductor interface structure formed on an n-type substrate. Ballistic electrons entering the semiconductor are swept away from the interface by the depletion layer potential. (b) Ballistic-hole spectroscopy of a metal-semiconductor interface structure formed on a p-type substrate. Ballistic holes entering the semiconductor are swept away from the interface by the depletion layer potential. The fundamental asymmetry between the collected carrier distributions for ballistic electron and hole spectroscopy is immediately apparent.

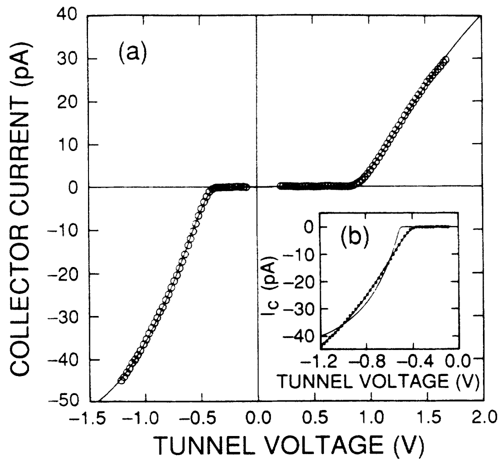

FIG. 2. Experimental (circle symbols) and theoretical (solid lines) ballistic carrier spectra for the Au/Si(100) Schottky-barrier interface. (a) Experimental ballistic-hole (negative tunnel voltage) and ballistic-electron (positive tunnel voltage) spectra measured at 77 K for p- and n-type substrates, respectively. The Au film thicknesses for the p- and n-type Schottky-barrier structures are 150 and 100 Å, respectively. The band gap, valence-band maximum, and conduction-band minimum at the subsurface semiconductor interface are clearly seen as thresholds in the hole and electron spectra. The theoretical spectra are in excellent agreement with the experimental results. The measured Schottky-barrier heights are $V_{bh}=0.35$ eV and $V_{be}=0.82$ eV. (b) Comparison of the ballistic-hole spectrum (dots) with a theoretical spectrum fit to the data and evaluated without the requirement of transverse momentum conservation on hole transport at the interface. The drastic discrepancy demonstrates the primary influence of transverse momentum conservation on hole interface transmission for this system.

entire apparatus including the liquid reservoir was contained in a flowing nitrogen gas environment. Ballistic-hole spectra are obtained by sweeping V, holding tunnel current constant (at 1.0 nA) under feedback control, and measuring collector current. The Au/Si(100) and Au/GaAs(100) Schottky-barrier interfaces were prepared by evaporation of Au in ultrahigh vacuum on chemically prepared[2] Si wafer substrates (n type, $n=2\times10^{15}$ cm^{-3} and p type, $p=3\times10^{15}$ cm^{-3}) and on molecular-beam epitaxy (MBE) grown, GaAs buffer layers (p-type, $p=3\times10^{16}$ cm^{-3}) deposited on p-type GaAs substrates.

Ballistic-electron and ballistic-hole spectra for the Au/Si(100) system are shown in Fig. 2(a). The combined spectra show a region of zero-observed collector current bounded by two abrupt thresholds in the current. The threshold for positive tunnel bias (tunnel tip negative with respect to the base) directly indicates the position of the conduction-band minimum. As expected, for negative tunnel bias, the observed collector current is *opposite* in sign to that observed for positive V. The observed current provides a spectroscopy of ballistic hole interface transport. Further, the ballistic-hole spectrum threshold directly yields the barrier height formed by the valence-band maximum at the subsurface Schottky barrier.

The detailed characteristics of ballistic-hole creation and transport are compared to those for ballistic electrons in the experimental derivative spectra of Fig. 3(a). The marked difference in spectral shape above threshold between the hole and electron derivative spectra reveals a fundamental asymmetry between tunnel spectroscopy of unoccupied (positive V) and occupied (negative V) states in the base electrode. As shown in Fig. 1(a), for both spectroscopies, the tunneling electron energy distribution is peaked at the source electrode Fermi level and decreases with decreasing energy, due to the decay of tunnel probability. For ballistic-electron spectroscopy at positive tunnel bias, the collected electrons originate from the *top* of the tunnel distribution where the distribution is maximum. The number of electrons created per unit energy remains nearly constant with bias. However, for ballistic-hole spectroscopy at negative tunnel bias, shown in Fig. 1(b), the ballistic-hole distribution originates from the *bottom* of the tunnel distribution where the distribution is at a minimum. Therefore, the number of holes created per unit energy *decreases* with increasing bias. This fundamental asymmetry between BEEM electron and hole spectroscopy is directly revealed in the experimental spectra of Fig. 3(a). The derivative spectra of Fig. 3(a) display the fine details of the collector current volt-

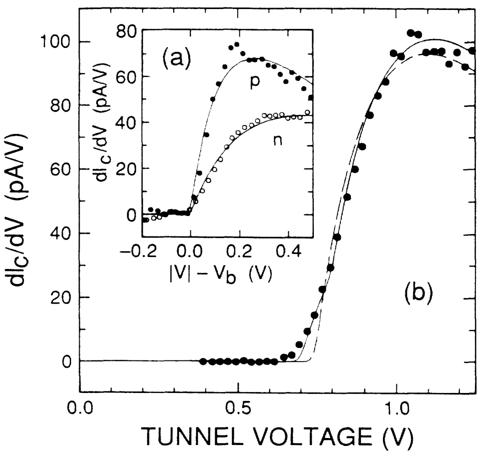

FIG. 3. Experimental and theoretical derivative ballistic carrier spectra for the Schottky-barrier structures measured at 77 K. (a) An experimental derivative ballistic-hole spectrum (dots) is compared to an experimental derivative ballistic-electron spectrum (open circles) for the Au/Si(100) Schottky-barrier interface. The asymmetry between hole and electron spectroscopies is apparent in the experimental spectra and is accurately described by theory (solid lines). (b) Experimental hole spectrum (solid circles) of the valence band of the Au/GaAs(100) Schottky-barrier interface. The Au film thickness for this structure is 100 Å. A theoretical spectrum for a single valence band (dashed line) is in disagreement with experiment. However, a theoretical spectrum for two valence bands (solid line) correctly reproduces the experimental result.

age dependence with great sensitivity. The ballistic-hole derivative spectrum displays an abrupt maximum and a sharp decay resulting from the decay in the ballistic-hole distribution with tunnel bias above threshold. Qualitatively different behavior is observed for ballistic-electron spectroscopy where a smooth increase is observed in the derivative spectrum. It is particularly significant that the accurate understanding of this contrasting behavior presents a sensitive and important test of interface transport spectroscopy and theory.

The ballistic-electron BEEM theory[3] is directly applicable to ballistic-hole spectroscopy. As for electron transport, conditions on hole interface transport are determined by the incident hole total energy and transverse momentum. Conservation of transverse momentum at the interface implies that for any hole energy below the valence-band maximum, hole interface transmission is allowed for angles of incidence less than a critical angle.[8] As shown for electron transport, the critical angle for hole transmission depends on incident hole energy, the discontinuity in effective mass at the interface, and the offset between the conduction-band minimum in the metal base and the valence-band maximum in the semiconductor collector. Since the incident hole energy is simply controlled by tunnel bias voltage, a direct spectroscopy of interface valence-band structure is enabled.

Experimental and theoretical BEEM spectra are compared in Fig. 3(a) for ballistic-electron and -hole spectroscopy of the conduction and valence bands, respectively, at the Au/Si(100) Schottky-barrier interface. The theoretical spectra for ballistic carrier spectroscopy are fit to the experimental results by varying only the Schottky-barrier height and an energy-independent transmission probability factor, R.[3] It is particularly significant that the shapes of the calculated spectra in the critical near-threshold region are *independent* of the adjusting parameters.[9] The contrasting behavior of ballistic-electron and -hole spectroscopies discussed above is accurately described by theory and detailed agreement with experiment is observed. Further, the theoretical fit to the experimental electron and hole spectra provide a direct measure of the Si band gap at the subsurface interface [clearly shown in Fig. 2(a)]. Excellent agreement is obtained between the band-gap value derived from the electron and hole transmission thresholds measured by BEEM, 1.18 ± 0.01 eV, and the bulk band-gap value for Si measured at 77 K by other methods, 1.17 eV.[6]

The critical properties of interface transport are revealed in ballistic-hole spectra with great sensitivity. This is demonstrated in Fig. 2(b) by the comparison of experimental spectra to theoretical spectra fit to the data and evaluated without the requirements of transverse momentum conservation at the interface. The drastic discrepancy demonstrates the primary influence of transverse momentum conservation on hole interface transmission for this system. However, the excellent agreement between experimental and theoretical derivative spectra including transverse momentum conservation for both ballistic-electron and -hole spectroscopies indicate that the dominant effects determining interface carrier transport have been probed by BEEM and are described theoretically.

Hole transport at semiconductor interfaces is of central importance for the understanding of the electronic properties of superlattice and quantum well structures. A particularly illuminating investigation of transport involves the comparison of ballistic-hole spectra for Si and GaAs interfaces. The Si valence-band maximum is composed of two bands of different effective mass, degenerate at the Brillouin-zone center (spin-orbit coupling can be neglected). Therefore, ballistic-hole spectroscopy of the Au/Si(100) interface valence-band structure reveals a single threshold at the valence-band maximum as shown in Figs. 2 and 3(a). In GaAs, spin-orbit coupling, which is an order of magnitude larger than in Si, splits the bands near the zone center into a heavy-hole band, a light-hole band, and a splitoff band. At larger k, the light- and heavy-hole bands are nearly parallel, having equal effective mass, $m^* = 0.5$.[10] Experimental ballistic-hole spectra for Au/GaAs(100) always show the threshold shape displayed in Fig. 3(b), directly reflecting this light- and heavy-hole splitting. Theoretical modeling shows that the splitoff band for both Si and GaAs would be difficult to observe experimentally because its lower mass results in a small critical angle for collection. In the case of GaAs, the 0.34-eV energy separation of the splitoff band places it at the maximum of the light- and heavy-hole derivative spectra, compounding the detection difficulty.

It is clear from Fig. 3(b) that the measured spectra are in disagreement with a theoretical treatment for a single band, but are in good agreement with a two-band model.

The observed splitting of the light- and heavy-hole bands of 0.10 ± 0.02 eV represents an average over the azimuthal angle which is to be compared to a calculated value for high symmetry directions of approximately 0.09 eV.[10] It is notable that phase space considerations alone[3] would not predict the observation of the light-hole band, since it presents no additional phase space for hole transmission. The observation thus implies that each band provides a separate channel for current collection, and hence the interface transmits less than 100% of the incident carriers within the critical angle of the heavy-hole band. This is most simply explained by noting that one channel (heavy-hole) involves only holes with $|m_j| = \frac{3}{2}$ while the other corresponds to $|m_j| = \frac{1}{2}$.

In summary, ballistic-hole transport properties of subsurface interfaces have been accurately characterized with a new, energy-resolved spectroscopy. The high resolution of this low-temperature spectroscopy provides a strict test of interface transport theory. Theoretical spectra show excellent, detailed agreement with the experimental results. Important applications of ballistic-hole spectroscopy have been described and others are anticipated because of the sensitivity and adaptability of this method to many materials, structures, and measurements. A significant advantage of this spectroscopy is its capability for high spatial-resolution and imaging capabilities. The ability to characterize local interface properties enables the identification and investigation of defects and also the identification and measurement of ideal interface regions.[2-4] In addition, ballistic-hole spectroscopy may be used for energy-resolved hole-transport investigations of thin metal films and semiconductor heterostructures.

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[8]The critical angle for hole transmission, θ_c, is defined by $\sin^2\theta_c = (m^*/m)[(|eV| - eV_b)/(E_F \pm |eV|)]$, where the sum and difference in the denominator applies to electron and hole transport [see Ref. 3], respectively. Also, eV_b is the familiar Schottky-barrier height between the base Fermi level and semiconductor valence-band maximum for holes (conduction-band minimum for electrons), and m^* and m are the effective masses of the collector valence band and base conduction band, respectively. With the introduction of this form for the critical angle, the theory of Ref. 3 is directly applicable to ballistic-hole transport.

[9]The shape of the spectral region well above threshold is weakly dependent on the values of the tunnel barrier height ϕ and the tunnel barrier width S, which determine the detailed shape of the electron tunnel distribution derived from planar tunneling theory. All ballistic-electron theoretical spectra are calculated with values of ϕ and S of 3 eV and 15 Å, respectively. However, best agreement is found for all cases between calculated and experimental ballistic-hole spectra for values of ϕ and S of 3 eV and 8 Å. The difference may result from the fundamental asymmetry of tunnel-barrier shape with tunnel bias resulting from the nonplanar vacuum tunneling geometry. [See J. A. Stroscio, R. M Feenstra, and A. P. Fein, Phys. Rev. Lett. **57**, 2579 (1986); R. M. Feenstra, J. A. Stroscio, and A. P. Fein, Surf. Sci. **181**, 295 (1987)].

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