Relation of Schottky Barriers to Empty Surface States on III-V Semiconductors*

D. E. Eastman and J. L. Freeouf
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
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We report new evidence that intrinsic surface states play a predominant role in determining Schottky-barrier energies for III-V semiconductors. Namely, empty surface-state levels have been measured (using photoelectron yield spectroscopy) for (110) GaSb, GaAs, GaP, InSb, and InAs whose one-electron energies correlate with Schottky-barrier energies reported by Mead and Spitzer. Also, these sharp molecularlike surface states are shown to be insensitive to metal overlayers and to be cation derived.

The nature of metal-semiconductor electrical barriers (Schottky barriers), which are of widespread technological and scientific interest,[1-8] has been discussed for many years. Bardeen[2] proposed that such Schottky barriers could be explained in terms of semiconductor surface states in the band gap, a model which has been widely adopted.[3,4] However, the physical basis for these states has been questioned[5] and alternative "continuumlike" theories involving metal-charge penetration[5,6] and screening[7] and polarizability[8] effects at the interface have been proposed and used in recent years. We present new results which support the former view,[2] i.e., that semiconductor surface states play a predominant role, rather than the latter views.[5-8]

In this paper we describe measurements of empty semiconductor surface states, both for the clean surface and in the presence of a metallic overlayer, that were made using a recently developed technique of photoemission partial-yield spectroscopy.[9,10] This technique, which is capable of measuring features in the photoabsorption spectrum for core-level excitations within an effective escape depth $l(E^*)$ (roughly 10–25 Å) of the surface,[9,10] shows promise as a spectroscopic probe of the solid-solid interface. We observe sharp cation-derived core-level–to–surface-state transitions for III-V semiconductors. Further, these surface-state transitions persist in the presence of metal overlayers. The one-electron energies of these surface states for the clean surface correlate well with metal-semiconductor–interface Fermi energies, i.e., Schottky-barrier energies, and support Bardeen's early explanation[2] of Schottky barriers. Before discussing the relation of intrinsic-surface-state energies to Schottky-barrier energies, we shall describe the cation-derived nature of these states and their lack of sensitivity to metal overlayers.

Photoemission partial-yield spectra [secondary-electron emission $N_{sec}(h\nu;E^*)$] for (110) GaSb are depicted in Fig. 1 for Ga($3d$) transitions (lower scale) and for Sb($4d$) transitions (upper scale). The energy scales have been displaced by the difference in Ga($3d_{5/2}$) and Sb($4d_{5/2}$) binding energies so as to line up one-electron energy positions for $d_{5/2}$ transitions. In Fig. 1, E_v and E_c denote the $d_{5/2}$ transition energies to the valence- and conduction-band edges, respectively. A sharp Ga($d_{5/2}$) transition to a surface-state level about 0.6 eV above E_v (at $h\nu = 19.3$ eV) is seen, together with a more intense Ga($d_{3/2}$) transition to this state ($h\nu = 19.8$ eV) which is separated by the Ga($3d$) spin-orbit splitting ($\Delta = 0.50$ eV). In contrast, no transitions to this surface state are

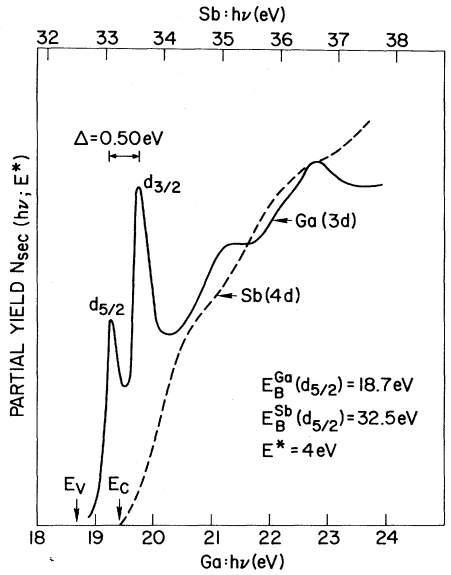

FIG. 1. Partial-yield spectra for (110) GaSb for Ga($3d$) transitions and for Sb($4d$) transitions. Only Ga($3d$) transitions into an empty-surface-state level at ~0.6 eV above E_v are observed.

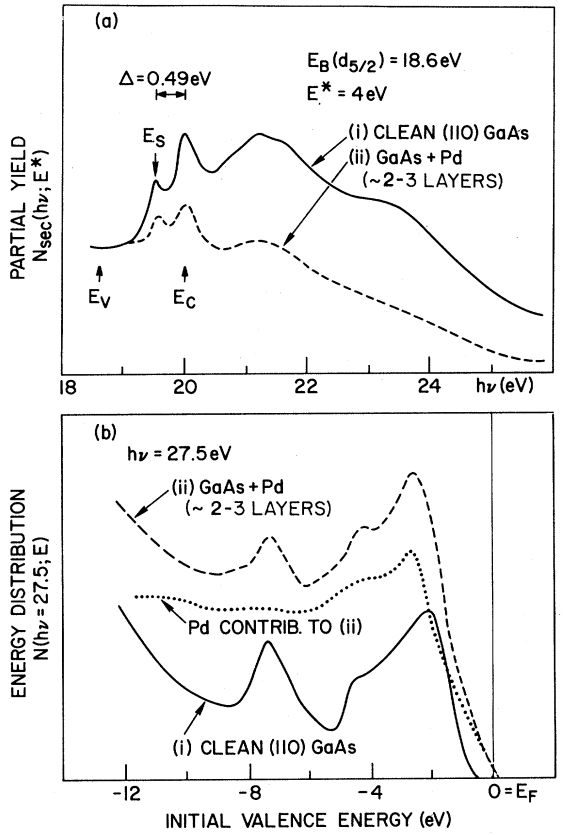

FIG. 2. (a) Partial-yield spectrum for clean (110) GaAs and for (110) GaAs covered with ~2–3 atomic layers of Pd. Both show transitions to a surface state ~0.9 eV above E_v. (b) Photoemission energy distributions for clean (110) GaAs and for (110) GaAs covered with ~2–3 atomic layers of Pd.

seen for Sb($4d$) transitions. Thus, these sharp, molecularlike, empty, surface states are seen to be cation derived, i.e., localized on the Ga atoms. Previously, Gregory *et al.*[11] have suggested, based on a bond-orbital model, that the empty surface states on (110) GaAs are cation derived in nature.

We have observed empty surface states on (110) GaAs to be insensitive to overlayers of Pd. Partial-yield spectra $N_{sec}(h\nu, E^*)$ for clean n-type GaAs and for GaAs plus Pd (~2–3 layers) are shown in Fig. 2(a), and energy distributions $N(E; h\nu = 27.5$ eV) for the corresponding surfaces are shown in Fig. 2(b). In Fig. 2(a), Ga($3d_{5/2}$) transitions (at $h\nu = 19.5$ eV) to a surface-state level at 0.9 eV above the valence-band edge are observed for both clean GaAs and for GaAs + Pd (~2–3 layers). Thus, the Pd overlayer is seen to have essentially no effect on the empty-surface-state level of GaAs other than an expected attenuation of emission intensity. We have observed similar results for In overlayers (up to ~20-Å thick) on GaAs, GaSb, and InAs.

The nature of this Pd overlayer is shown in Fig. 2(b), where photoemission energy distributions curves [*i* and *ii*] are normalized to the incident photon flux. The Pd overlayer doubled the total emission intensity and resulted in no change (< 0.05 eV) in band bending.[12] The Pd contribution to curve *ii* (GaAs + Pd), was determined by subtracting an attenuated GaAs spectrum; this attenuation (~× 0.5) was determined by measuring the attenuation of the Ga($3d$) core level. The Pd-overlayer spectrum (dashed curve) is characteristic of a broad resonant bound-state $4d$ level with a peak near − 2 eV and a metallic edge at the Fermi level E_F, and is not characteristic of bulk Pd. This observation, together with the low surface diffusivity of Pd at room temperature, suggests that Pd is deposited as a fairly homogeneous overlayer.

We now present a summary of these cation-derived molecularlike empty surface states that have been measured for GaSb, GaAs, GaP, InSb, and InAs, and compare their one-electron energies with the corresponding Schottky-barrier energies for Au contacts reported by Mead and Spitzer.[13] In Fig. 3, E_s denotes the measured one-electron energy of the surface-state transition peak, the solid triangularlike curve roughly denotes the measured width of this transition (including core-level broadening), and E_F denotes the Fermi level at the surface (n-type samples). Thus E_F roughly denotes the low-density edge of these surface-state levels. No filled surface states were observed between E_F and the top of the bulk valence bands (E_v). The dashed lines schematically represent the bulk valence- (cross hatched) and conduction-band densities of states, with edges at E_v and E_c, respectively (E_v and E_c energies given). The lowest-lying conduction-band edges L_1 and X_1 are also denoted; these were determined from the band calculations of Cohen and Bergstresser[14] fit to optical data together with photoemission valence-band densities of states.[15] We observe that the surface-state levels E_s bear no obvious relation to E_c for direct-gap semiconductors, but rather systematically shift with the low-lying conduction-band states L_1, X_1. In GaSb, GaAs, and GaP, the surface-state levels lie in the bulk band gap, with E_s shifting from near the top of the gap in GaSb to near the middle of the gap in GaP. In contrast,

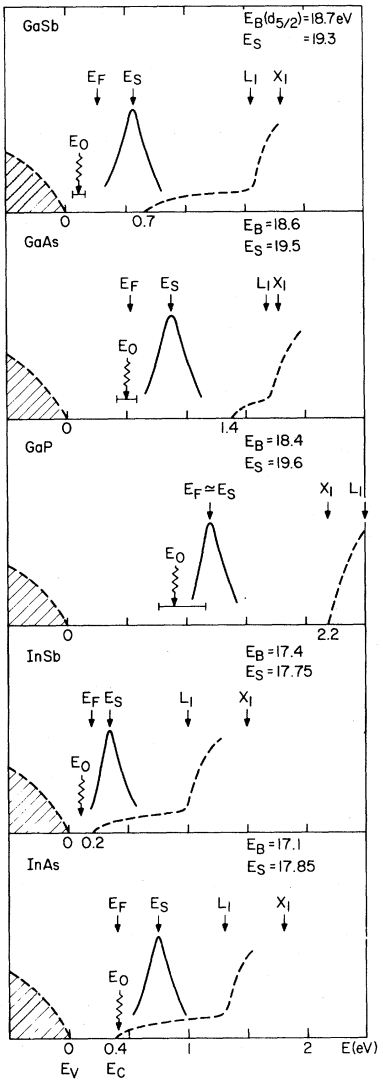

FIG. 3. Summary of empty-surface-state levels observed for (110) GaSb, GaAs, GaP, InSb, and InAs. E_s and E_F denote the peak energy and Fermi energy at the surface for clean n-type samples. The Fermi levels (E_0) of gold metal contacts (Ref. 12) are seen to lie just below the surface-state levels.

InSb and InAs exhibit surface-state levels that occur above the bottom of the conduction band, with E_s being about 0.4 eV above E_c in InAs.

The Fermi levels (E_0) of gold contacts on these semiconductors as determined by Mead and Spitzer[13] are also summarized in Fig. 3, together with the range of Fermi energies for a number of metal contacts[13] (bracketed line). Thus $E_c - E_0$ denotes the electrical barriers (Schottky barriers) for these metal-semiconductor interfaces.

We note the striking observation that these metal-contact Fermi levels (E_0) always lie just below the low-energy edge (E_F) of the *intrinsic* surface-state levels we have observed for the clean surfaces. This not only occurs for GaAs and GaP, which obey the "$\frac{2}{3}$ bandgap" rule[1,13] for Schottky-barrier energies, but also for GaSb, which is somewhat anomalous, and for InAs, a notable exception which has no Schottky barrier.[13] The latter behavior is consistent with the surface-state level lying well above E_c, i.e., these surface states are essentially precluded from affecting the Schottky-barrier energy.

Note that we are using an observed optical transition energy and a measured binding energy to obtain a one-electron energy for these surface states. The narrow linewidths for core-level transitions into these cation-derived molecular-like surface states suggests that electron-hole correlation effects might be important.[16] Namely, relative to a one-electron picture, a Coulombic electron-hole attraction would decrease the surface-state transition energy, while the changes in screening due to a localized excited state would tend to increase the apparent surface-state energy. The magnitude of these effects has not yet been established, but data for (111) Ge,[9] together with surface-state optical data,[17] suggest that these correlation effects are possibly less than ~ 0.1–0.2 eV.

These possible correlation effects notwithstanding, the above correlation (Fig. 3) of cation-derived empty-surface-state-level energies with Schottky-barrier energies, together with our observed insensitivity of these surface states on GaAs to Pd overlayers, suggests that intrinsic molecularlike semiconductor surface states play a predominant role in determining Schottky barriers on III-V compound semiconductors. These surface states are envisioned as electrostatically excluding the Fermi level from the upper part of the bulk band gap (with the notable exception of InAs), and therefore the Schottky-barrier level E_0 lies in the low-energy tail of these surface states. Of course the energy position of this low-energy tail of surface states could be modified (e.g., by hybridization, screening, etc.) by the presence of metal overlayers; surface defects could also be important. This result supports the early suggestion of Bardeen[2] and is consistent with the surface-state interpretation of Mead[13] and Levine.[4] The surface-state model of Gregory *et al.*[11] for the clean surface is more accurate than the nearly-half-filled-band models[2] in light of the cation-derived nature of the empty-surface-

state levels we have observed. Alternate models involving metal-charge penetration,[5,6] band distortion due to interface screening effects,[7] surface polarizability,[8] and new metal-induced interface states[18] appear not to represent the major contribution to metal-semiconductor Schottky-barrier energies ($E_c - E_0$), but possibly are important in determining changes in barrier energies ($E_c - E_0$) for different metal contacts, and for trends observed as a function of semiconductor ionicity.[1,19]

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Dielectric Anomaly and the Metal-Insulator Transition in *n*-Type Silicon*

T. G. Castner and N. K. Lee
University of Rochester, Rochester, New York 14627

and

G. S. Cieloszyk† and G. L. Salinger
Rensselaer Polytechnic Institute, Troy, New York 12181

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Results from capacitance measurements on *n*-type silicon versus donor concentration show the onset of a possible divergence (polarization catastrophe) in the static dielectric constant at a critical concentration N_c, which is donor dependent, as N_c is approached from the insulating side. A substantial deviation from Clausius-Mosotti behavior occurs as $N \to N_c$.

Significant interest and controversy in recent years has surrounded the study of metal-insulator (M-I) transitions in solids and liquids. It has been difficult to establish in particular cases whether the transition results from electron-electron correlations, as originally proposed by Mott,[1] or whether other mechanisms are responsible. A wide variety of experimental techniques from transport measurements to NMR have been employed to study M-I transitions in transition metal oxides, metal ammonia solutions, alkali atoms in inert matrices, and heavily doped semiconductors.[2] One experimental quantity which has received little attention is the dependence of the static dielectric constant ϵ as the transition is approached from the insulating side. Since ϵ plays a key role in the binding of electrons by Coulombic potentials it is worth ascertaining the