Correlation for III-V and II-VI Semiconductors of the Au Schottky Barrier Energy with Anion Electronegativity*

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The Schottky barrier for holes on common III-V and II-VI semiconductors contacted by Au is shown to depend only on the anion electronegativity.

Variations in the heights of the electrical barrier between metals and semiconductors have been the subject of much experimental and empirical work.[1] In this Letter, we point out a heretofore unnoticed correlation between the Schottky barrier energy for Au on common III-V and II-VI semiconductors and the electronegativity of the anion of the semiconductor. This correlation applies to the zinc blende and wurtzite structures in which these semiconductors occur. Throughout this report, we will deal with data for Schottky barriers formed by intimate contact between a metal and a semiconductor in which no chemical reaction has taken place.

Previous work on this type of barrier has been summarized in a series of empirical rules. Mead and Spitzer[2] have shown that for covalent semiconductors, the barrier energies were relatively independent of the particular metal, and the value of the barrier for electrons was approximately two-thirds of the energy gap (the "two-thirds" rule). There have been a number of exceptions to this rule. Mead and Spitzer pointed out that InAs, GaSb, and InP all deviated from the two-thirds rule; Rideout[3] has noted a deviation in the $GaAs_{1-x}P_x$ alloys.

Mead[4] and Kurtin, McGill, and Mead[5] demonstrated a distinctly different variation of the barrier behavior on ionic insulators as contrasted with covalent semiconductors. For the ionic insulator, the barrier energies are found to vary strongly with the particular metal; while in the covalent semiconductor, the barrier energies are found to be approximately independent of the particular metal. The separation between the two types of behavior occurs abruptly at an electronegativity difference between the anion and cation of the binary compound of 0.6 (the "ionic-covalent" transition).

Analogous studies of the vacuum-semiconductor interface contribute to the understanding of the Schottky barrier. The ionization potential for the former interface, i.e., the energy difference between vacuum and the semiconductor valence-band maximum, has been shown by Swank[6] to depend on anion electronegativity in a way qualitatively similar to the present results. The recent photoemission measurements[7,8] of empty surface states on various III-V semiconductors indicate a correlation between Schottky-barrier height on covalent semiconductors and the low-energy edge of the distribution of empty surface states.

In this Letter we would like to demonstrate that the Schottky-barrier energy between the Fermi level of the Au and the valence-band maximum of the semiconductor depends only on the particular anion in the semiconductor. Furthermore, the magnitude of the barrier increases monotonically with increasing anion electronegativity.[9] This trend is found to persist across the ionic-covalent transition.

Figure 1 displays experimental values for Schottky barriers as reported in a 1966 compliation[10] and more recently.[11-21] The data presented cover the common[22] III-V and II-VI semiconductors with the exception of the Al compounds.[23] Some of the measurements were made on interfaces prepared under rather optimum conditions, e.g., vacuum cleaving in a stream of evaporating Au. In other cases, e.g., the GaP data, a wide variety of surface preparations and crystal orientations are represented.

The usual relation, $\varphi_n + \varphi_p = E_g$, where φ_n is the barrier on n material, φ_p the barrier on p material, and E_g the energy gap, is seen to be confirmed within experimental uncertainties where both φ_n and φ_p are known. Where only φ_n or only φ_p is known, this relation has been used to locate band edges. In this way the band edge energies for this group of compounds may be intercompared. To facilitate comparisons the compounds are presented in order of increasing anion electronegativity to the right. Further data would be desirable for this plot, and we are presently investigating the Hg chalcogenides.

Figure 1 demonstrates that the barriers for holes for different compounds involving the same anion are very nearly equal. For example, both
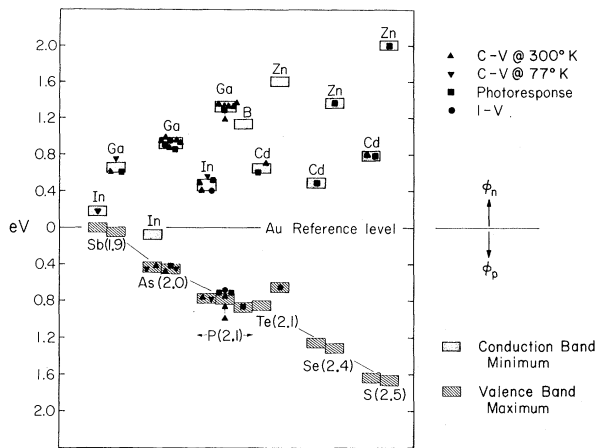
FIG. 1. Heights of Schottky barriers produced by Au on III-V and II-VI semiconductors. The reference energy in the plot is the Fermi energy of the Au contact. The data points indicate the experimental method used and were taken from the compilation of Ref. 10, supplemented as follows: InAs (Refs. 11, 12), n-GaAs (Refs. 12–15), n-InP (Ref. 16), p-GaP (Ref. 17), n-GaP (Refs. 17–20), and p-ZnTe (Ref. 21). At each cluster of data points is located the appropriate band edge. Where no data are available, band edges are located as discussed in the text. The cations and anions of each compound are labeled next to a band edge, and the Pauling electronegativities of the anions are listed.

FIG. 2. Comparison of the energy of the valence band maximum, as estimated in the previous figure, with the electronegativity of the anion.

GaAs and InAs have barriers which are approximately 0.45 eV below the Au Fermi level. Similar results are indicated for the antimonides, phosphides, tellurides, selenides, and sulfides. On the other hand, the location of the conduction band with respect to the Au reference level fluctuates widely for different cations and the same anion. Further, for the same cation and different anions, the position of the valence-band maximum is not constant.

In addition, the data show that the electronegativity of the anion is a good indication of the location of the valence-band maximum with respect to the Au reference level. Averaging the location of the valence-band maxima from Fig. 1 for a particular anion, one obtains the results exhibited in Fig. 2, where electronegativity is the abscissa. This figure shows that the location of the average valence-band maximum is an approximately linear function of the anion electronegativity.[9] Further, in the case of phosphorus and tellurium which have the same electronegativities on the Pauling scale,[9] the averaged valence-band maxima almost coincide. Swank[6] reported an analogous dependence for the vacuum-semicon-
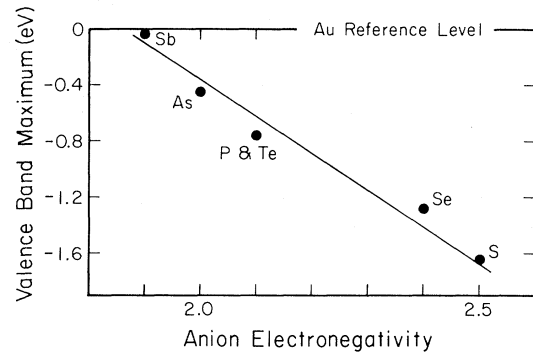
ductor interface, the linear slope being ~37% greater for that interface compared to the Au-semiconductor interface treated here, but with greater scatter in the data about the line.

This correlation is a remarkable one. It encompasses not only those materials which agree with the old two-thirds rule but also those materials which deviate from it strongly, such as InAs. Further, the correlation persists across the ionic-covalent transition where the mechanism for determining the position of the Fermi level at the surface of the semiconductor is thought to change dramatically. InSb, InP, and GaAs are distinctly on the covalent side of the transition while ZnS is distinctly ionic.

Similar correlations, but with more scatter in the location of the valence-band maxima, have been noted for Ag and Cu replacing Au.[24] However, we would expect the correlation to disappear for very electropositive metals.

This correlation suggests that the energy position of the top of the valence band with respect to the Fermi energy of the Au is determined in large part by the anion. Further, the valence-band maxima of these materials are derived primarily from the p-like atomic states[25-28] of the anion. Chadi and Cohen[26] find in their tight-binding calculation for GaAs and ZnSe that the valence-band maximum is located within 0.2 eV of their value for the energy of the anion p level. Using the same parameters as they used in their tight-binding calculation, we computed the ratio of the square of the wave function on the anion to that on the cation. At the valence-band maximum, we find that this ratio is 24 for GaAs and 60 for ZnSe. While the tight-binding calculation may somewhat overestimate the anionic character of

the top of the valence band, other evidence for the strongly anionic character of the valence-band maximum is provided by (1) the bond-orbital calculations of Harrison and co-workers[28]; (2) the fact that the filled surface state on GaAs[29] has been found to be primarily anion derived and located near the top of the valence-band maximum; and (3) the fact that the spin-orbit splitting at the top of the valence band in the III-V and II-VI semiconductors depends more heavily on the atomic spin-orbit splitting of the anion than the atomic spin-orbit splitting of the cation.[30] Hence, the valence-band maximum corresponds to eigenstates which are primarily centered on the anion. The electronegativity of the anion provides a chemical measure of the position of bond-producing atomic states, such as the p-like atomic state. Hence, we expect the type of correlation reported here between the valence-band maximum relative to a common reference level and the anion electronegativity. We are currently exploring this proposal and its implications for the theory of various heterostructures.[31]

[1]See, for example, C. A. Mead, Solid State Electron. 9, 1023 (1966); T. C. McGill, J. Vac. Sci. Technol. 11, 935 (1974), and the references contained therein.

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[9]Throughout this discussion we used Pauling's electronegativity scale; see L. Pauling, The Nature of the Chemical Bond (Cornell Univ. Press, Ithaca, N. Y., 1960), 3rd ed., p. 93. However, similar results were obtained using the Phillips scale; see J. C. Phillips, Bonds and Bands in Semiconductors (Academic, New York, 1973), p. 54. The only difference was in the ordering of the tellurides.

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[23]Aluminum compounds have been omitted since their surfaces are quite reactive; barriers (Ref. 9) reported on n-AlAs and p-AlSb do not follow the trends discussed in this Letter. Also pertinent to this singularity is the common placement of Al in column IIIB rather than IIIA. See, for example, L. Pauling, The Nature of the Chemical Bond (Cornell Univ. Press, Ithaca, N. Y., 1960), 3rd ed., pp. 93 and 410.

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