

Schottky barriers on compound semiconductors: The role of the anion*

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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. Compilation of the experimental data shows that compound semiconductors with the same anion but different cations possess very similar values for the the Au Schottky barrier for holes. Further, the data show that the Pauling electronegativity of the anion provides a useful ordering parameter for the height of the Schottky barrier. This correlation is compared with analogous barrier data on rocksalt and layer structures as well as earlier results for the semiconductor-vacuum interface.

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I. BACKGROUND

Some eleven years ago Aven and Mead showed, in their study¹ of Schottky barriers on CdS and ZnS, that the barrier heights of these two materials differed by the same energy as did their band gaps. The relationship was observed to hold independently of which of a variety of metals was used as a contact to the two semiconductors, and it indicated that the valence bands of the two materials were bending to the same energy position at the metal interface. The bands in both the bulk and at the surface of the two semiconductors are sketched in Fig. 1, which is scaled for the case where the contact metal is Au. Although the two valence bands have different energies in their respective bulk semiconductors, the band bending near the metal interface is just sufficient to bring the two valence bands to the same energy level at the interface. They found their observation "... not surprising since the valence band can be identified with a sulfur ion in each case."

Subsequently, Swank² made analogous measurements for semiconductor-vacuum interfaces, studying not only sulfides but selenides and tellurides as well. He found that the "... photoelectric threshold is determined primarily by the chalcogen." Otherwise stated, he found that the ionization potential Φ (i.e., the energy difference between the valence band maximum and the vacuum level) was primarily determined by the anion in the compound.

More recently, Kajiyama *et al.*³ measured the barrier height of electrons ϕ_n for Au contacts to *n*-type GaAs-InAs alloys. Their measurements indicated that ϕ_n tracked the band gap E_g fairly accurately across the alloy system. This result implies that the barrier height for holes ϕ_p is almost independent of the Ga/In ratio in these alloys, as indicated in Fig. 2. Since the specific cations Ga and In apparently do not play a role in determining ϕ_p , one wonders whether the constant anion As is not associated with the constancy of ϕ_p .

II. SCHOTTKY-BARRIER DATA ON III-V AND II-VI COMPOUNDS

Recently the present authors undertook a general examination of measured barrier heights on compound semiconductors. A brief account⁴ of the examination has been presented elsewhere; the present report aims to give a more general overview of the data that was analyzed. Early in our examination of the data it became apparent that the contact metal most extensively studied was Au, and that most investigations seeking to define carefully and reproducibly the experimental conditions utilized Au contacts. In some respects Al contacts have been comparably studied, but Al is considerably more chemically reactive and we wanted to deal with the ideal Schottky barriers formed by intimate contact between a metal and a semiconductor in which no chemical reaction has taken place. Hence the scope of the examination was limited to Au contacts.

Another feature of the barrier data that became evident was that measurements were, with a few exceptions to be noted, made primarily on the common tetrahedral compounds, the III-V's and II-VI's. This concentration of measurements on a few materials enables conclusions to be drawn about the role of the anion in common III-V and II-VI compounds with fair confidence. On the other hand, classes such as the sixfold coordinated (i.e., rocksalt structure) semiconductors remain much in need of further investigation.

The compilation of barrier data that we accumulated appears in Fig. 3, with the III-V data to the left and the II-VI data to the right. Within the III-V compounds, the antimonides appear first, followed by the arsenides, in turn followed by the phosphides (i.e., with the anions in ascending order up column V). The II-VI compounds are arranged similarly, with anions in ascending order in column VI. The same ordering of these compounds is given by the Pauling electronegativity,⁵ as will be discussed later.

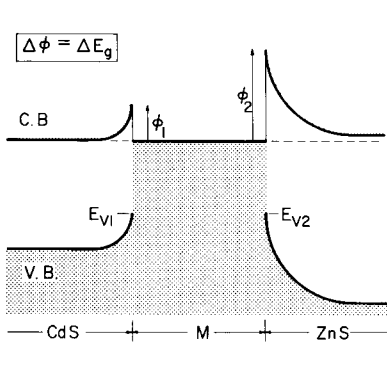


FIG. 1. Conduction and valence band energies for metal contact on CdS and ZnS, according to Aven and Mead, Ref. 1. The difference in the Schottky barrier heights ϕ_1 and ϕ_2 is matched by the difference in band gaps, leaving the valence band energies, E_{V1} and E_{V2} , equal at the interfaces with metal M. Figure is scaled to show barrier heights when metal M is Au.

The most important feature of Fig. 3 is that the barrier for holes, ϕ_p , depends almost entirely on the anion alone, i.e., the cation plays little, if any, role. Thus the role of the anion in Schottky barriers suggested in the earlier work just discussed appears to be quite general. One can then speak of semiconductors contacted by Au as having an energy difference from the Au Fermi level to the semiconductor valence band of ~ 0.8 eV for phosphides, ~ 0.4 eV for arsenides, etc.

The data of Fig. 3 also allows a check of a relation commonly assumed in barrier studies, namely that the sum ($\phi_n + \phi_p$) is equivalent to the band gap E_g . Physically this relation derives from the assumption that the energy relationships at a Schottky barrier are independent of bulk doping; otherwise stated, if the positions of band edges at the barrier are the same for p or n material, one readily sees from a sketch that this relation holds. The relation may be tested in Fig. 3 for any materials where both ϕ_n and ϕ_p are known. In fact, the relation holds well within experimental error for the data in the figure. An interesting aside is that when ϕ_n and ϕ_p values from the same author are intercompared, their sum comes appreciably closer to E_g than when the whole set of ϕ_n and ϕ_p values for a given material are considered. This improvement in accuracy probably results from the greater consistency in experimental technique within a single experimenters measurements.

For some materials, only ϕ_n or only ϕ_p is known. In most instances where this is so, the unknown barrier would be quite hard to measure. For example, the barrier may be too low, as in the p -type antimonides or n -InAs. In these cases a Au contact is known to be a very good ohmic and ordinarily one considers that there is no barrier present at all. In other cases, the semiconductor cannot be rendered sufficiently conducting for reliable barrier height determination; this is true of n -ZnTe and the p -selenides and p -sulfides. Where there is a missing barrier height in the data collection, we have estimated the unknown barrier from the above relationship and included it in the plot.

The scatter in the data of Fig. 3 deserves some mention. Mostly the scatter arises from the great variety of experimental techniques used. For example, the barrier height measurements on n -GaAs encompass all three principal experimental methods, were performed on both polar and nonpolar crystal faces which were prepared by a variety of procedures including cleaving in vacuum in a stream of evaporating Au, and are the result of five independent investigations. The range of this data is somewhat less than 0.2 eV. On the other

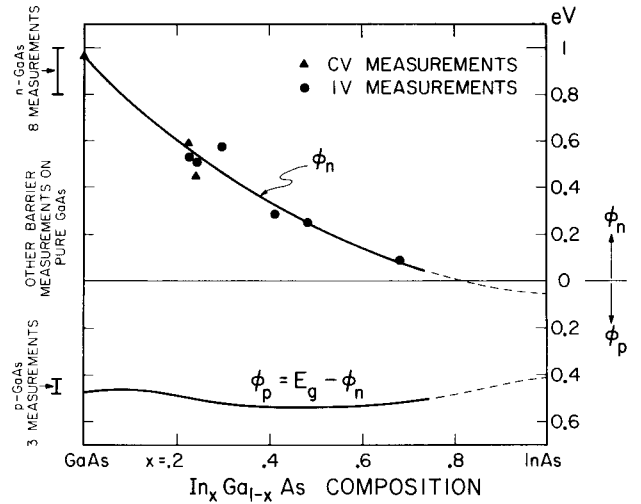


FIG. 2. Measured barrier heights ϕ_n and calculated barrier heights ϕ_p produced by Au on $In_xGa_{1-x}As$. The ϕ_n data is from Kajiyama *et al.*, Ref. 3. Barrier heights on pure GaAs, shown in detail in a later figure, are summarized at the left of this figure for comparison.

hand, with less variety in experimental parameters, a single investigator often gets reproducibility to within about 0.1 eV. The measurements on n -type chalcogenides were performed by the same investigator on (110) faces cleaved in vacuum evaporating Au, and all include a photoresponse measurement. The internal consistency of this data should be relatively good.

Finally we should mention that the data collection in Fig. 3 omits two Al compounds for which barrier data has been presented,⁶ namely, AlAs and AlSb. The barriers reported for these two materials are not consistent with the arsenide and antimonide barriers presented in Fig. 3. A likely reason for this discrepancy is the well-known reactivity of these Al compounds. Regarding their reactivity with Au, recent evidence⁷ on Au-based contacts to $Ga_{1-x}Al_xAs$ is relevant: "With $Ga_{1-x}Al_xAs$ the contact behavior appears to be very sensitive to the Al concentration and difficulties increase as the Al mole fraction x increases."

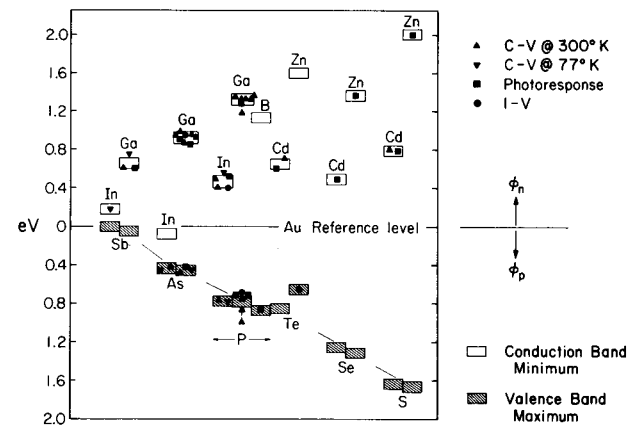


FIG. 3. Barrier heights produced by Au on common III-V and II-VI semiconductors. The experimental techniques used for each data point are indicated in the upper right corner, and the sources for the data are listed in Ref. 4.

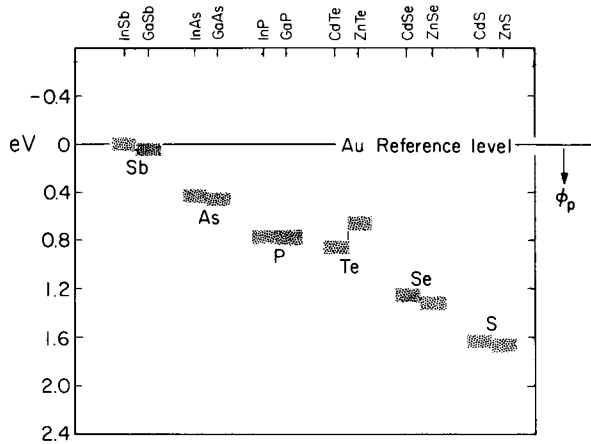


FIG. 4. Simplification of Fig. 3 to show the barrier ϕ_p as a function of the anion present.

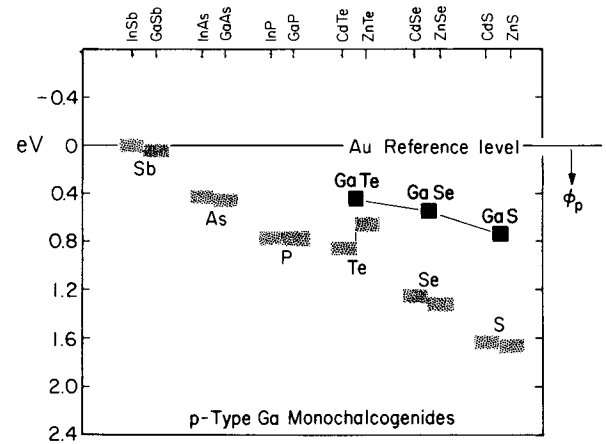


FIG. 5. Barrier heights ϕ_p for a family of layer compounds, the Ga monochalcogenides, compared to barrier heights on tetrahedral compounds.

III. OTHER RELATED MEASUREMENTS

For the purpose of comparing the results in Fig. 3 with other measurements, we use the simplified version presented in Fig. 4. Only the approximate height of the barrier ϕ_p is indicated in this figure for each of the common compound semiconductors just discussed.

A. Rocksalt compounds

The common III-V and II-VI compounds previously discussed have approximately tetrahedral, i.e., fourfold, coordination. Those with zincblende structure are exactly tetrahedral, whereas the wurtzite structures are slightly distorted from tetrahedral. Perhaps the second most important crystal structure adopted by binary semiconductor compounds is the sixfold coordinated rocksalt (i.e., NaCl) structure. The Pb chalcogenides appear in this structure, and other semiconductors, e.g., cinnabar, appear in distorted versions of the structure. The characterization of various metal contacts to PbTe by Nill et al.⁸ indicates that this compound would lie close to the Au reference level in Fig. 4. Its bandgap is ~ 0.2 eV so its valence band maximum is evidently positioned considerably higher in Fig. 4 than that of the tetrahedrally coordinated tellurides. Any possible generalization about valence band positions in this important class of semiconductors, however, awaits further barrier-height measurements.

B. Layer compounds

Another class of semiconductors for which barrier data exists is the Ga monochalcogenides. These are layer compounds, radically different from either of the above two structures. The barriers on the *p*-type compounds,⁹ indicated in Fig. 5, are substantially lower than the corresponding barriers on *p*-type II-VI compounds. Some insight into the cause of this is afforded by the band calculations of Schlüter,¹⁰ who concludes that the valence band maximum in GaSe is constituted of approximately equal contributions from cation and anion. By contrast, the valence band maxima in GaAs and ZnSe, both tetrahedral semiconductors, are composed predominantly of *p*-like atomic states on the anion.⁴

C. Semiconductor/vacuum interfaces

The ionization potential Φ at the vacuum interface of the common tetrahedral compounds is indicated in Fig. 6 and comes from the 1967 paper of Swank,² which includes data from some earlier investigators. For comparison with the present barrier data, some assignment has to be made for the work function of Au. A value of $W_F = 5.1$ eV was adopted as being consistent with recent investigators as well as Swank. We note, however, that Swank² reported values of W_F ranging from 5.08 to 5.59 eV in the course of his measurements. Perhaps this variability in W_F of the reference material is the reason that the many subsequent investigations at vacuum interfaces report only relative values, whereas absolute measurements like Swank's would be so useful to the comparisons needed for the present discussion.

Two features of Fig. 6 stand out. First the ionization potential, Φ , exhibits the same monotonic trends as the barrier ϕ_p . Thus the sequence of anions in the semiconductor compounds in Fig. 6 provides good ordering for both types of interface: semiconductor/Au and semiconductor/vacuum. Secondly, the range in Φ produced by this sequence of anions is greater than the range in ϕ_p . One can speculate that the relatively smaller sensitivity of ϕ_p to the anion results from

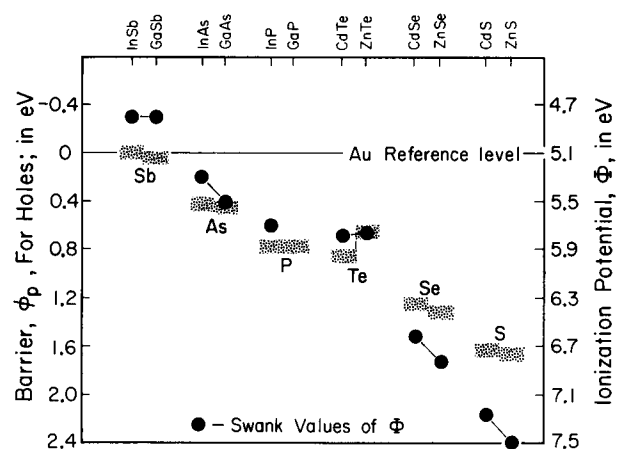


FIG. 6. The ionization potential Φ reported by Swank compared to the present values of the barrier heights ϕ_p . Assumed work function of Au is 5.1 eV.

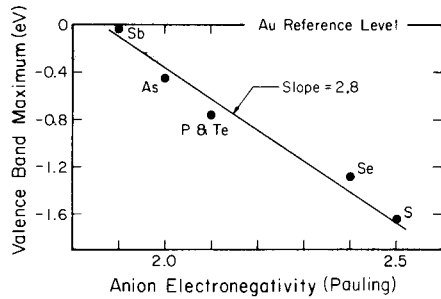


FIG. 7. The barrier heights of Fig. 4 as a function of the Pauling electronegativity of the anion.

the ability of the metal contact to screen electric fields emanating from the semiconductor. In any case, the similar effects of the anion on these interfaces, which are seemingly so very different, is striking.

IV. ANION ELECTRONEGATIVITY AS A MEASURE OF ϕ_p

The ordering of semiconductors in Fig. 3 and subsequent figures has not yet been emphasized in the present discussion, so that attention could be focused on intercomparing compounds with a common anion. However, the trends already evident in these figures make comparisons between the different anions interesting. To make such comparisons quantitative, we use the anion electronegativity as abscissa.

When the Pauling electronegativity of the anion is used as abscissa, the barrier data for the tetrahedral semiconductors can be summarized as in Fig. 7. Considering that the Pauling electronegativity is defined to only two significant figures, the trends exhibited by the data in the figure are fairly smooth, so we indicate an average slope of 2.8 to characterize the trend.

It is natural then to wonder if the slope of 2.8 can be extended to a greater range of electronegativities χ . The difficulty here lies in the paucity of suitable tetrahedral semiconductors. Two such semiconductors have been characterized, however, as is shown in Fig. 8. The single measurement⁶ that has been reported on a tetrahedral nitride, was performed on *p*-BN contacted by Au and yielded $\phi_p = 3.1$ eV. Thus this single datum, as is evident in Fig. 8, does come close to the extrapolated trend line from the previous figure. However, other suitable nitrides need to be characterized before deciding whether nitrides show the consistency noted earlier for the more common III-V and II-VI compounds.

The other additional semiconductor shown in Fig. 8 is ZnO. Measurements¹¹ of the barrier height ϕ_n for Au contacts on

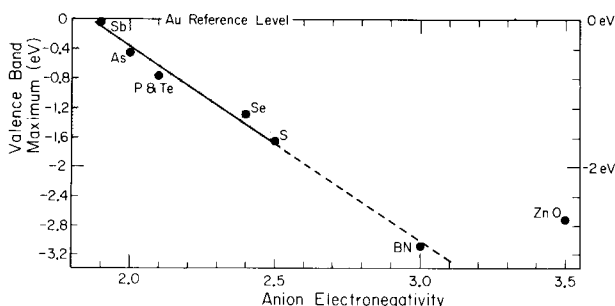


FIG. 8. Extension of the previous plot to include a much wider range of electronegativities.

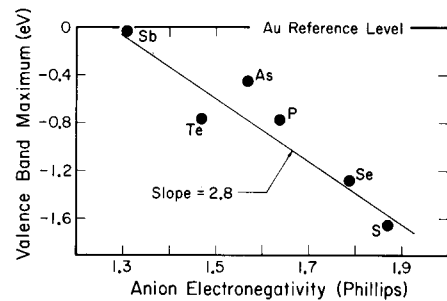


FIG. 9. The barrier heights of Fig. 4 as a function of the Phillips electronegativity of the anion.

n-ZnO, together with its band gap, imply $\phi_p \cong 2.7$ eV, as plotted in Fig. 8. ZnO clearly has a lower barrier ϕ_p than an extension of the trend line would have indicated. In this respect it is reminiscent of the nontetrahedral semiconductors discussed earlier. Probably more relevant, however, is that whatever mechanisms cause the anion to largely determine Schottky-barrier height in the common III-V and II-VI materials is no longer effective for ZnO.

Another electronegativity scale has been proposed,¹² and we show the barrier data for tetrahedral semiconductors plotted against the Phillips electronegativity in Fig. 9. The overall trend is the same as in Fig. 7, with slope = 2.8. However, the phosphides and tellurides, which we find to have approximately the same barrier height ϕ_p have substantially different electronegativities on the Phillips scale.

V. DISCUSSION

The experimental data reported above strongly suggest that, in the common III-V and II-VI semiconductors, the energy position of the maximum in the valence band is determined strictly by the anion in the compound. These semiconductors all possess crystal structures which are tetrahedrally bonded zincblende or wurzite. In these materials the top of the valence band is at $k = 0$ and is predominately *p*-like in character.¹³ Further, tight binding calculations¹⁴ for GaAs and ZnSe suggest that the square of the ratio of the anion to cation contributions to the wave function at $k = 0$ is 24 and 60, respectively. This result shows that the top of the valence band is heavily weighted to the *p*-like state on the anion. Other evidence for this assertion is provided by strong dependence of the spin-orbit splitting at the top of the valence band on the anion and rather weak dependence on the cation.¹⁵ Recent experiments to determine the position of filled surface states on GaAs show that they are primarily anion derived and located near the top of the valence band.¹⁶

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, either the Au Fermi level or the vacuum level, and the anion electronegativity.

The layered compounds, GaS, GaSe, and GaTe, provide a test of this explanation for the above reported correlations. While these materials have as constituents anions which are contained in the III-V and II-VI compounds studied here, the structure and electronic spectra are quite different. Band

structure calculations for GaSe¹⁰ show that the energy states at the top of the valence band possess approximately equal amplitudes to be on the anion and cation. Hence, we would expect that the energy position of the top of the valence band to be rather different from that found in the III-V and II-VI compounds with the same anion. Further, the experimental data show that ϕ_p does increase with increasing anion electronegativity in the sequence CaTe, GaSe, and GaS, but at a much slower rate than is found in II-VI compounds. This behavior is what one would expect in a case where the cation plays a significant role.

The simple II-VI compound which does not fall on the straight line relating the value ϕ_p for Au to the anion electronegativity (see Fig. 8) is ZnO. While we do not have a detailed explanation for this result, measurements of the spin-orbit splitting at the top of the valence band in ZnO suggest a significant contribution from the *d* states of the Zn.¹⁷ As in the case of the layered compounds, this contribution from cation would tend to reduce the dependence of ϕ_p on the anion electronegativity and may provide an explanation for the deviation noted.

The concept of an energy position of the top of the valence band in the III-V and II-VI semiconductors which depends almost totally on the anion electronegativity should be of value in assessing the relative position of electronic states in other heterostructures involving these materials. For example, we expect that this concept will be useful in predicting the value of discontinuities in bands at semiconductor-semiconductor interfaces. Support for this view is provided by the studies on

Al_xGa_{1-x}As heterostructures.¹⁸ In these systems which have a common anion (As) the discontinuity in the valence band is found to be small in comparison to that in the conduction band. We are currently exploring this point and will deal with it in a separate publication.

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