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Chemical trends in metal-semiconductor barrier heights

M. Schlüter
Bell Laboratories, Murray Hill, New Jersey 07974

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Experimental data on metal-semiconductor interfaces are reexamined. It is found that the previously reported abrupt transition between covalent and ionic semiconductors is not that clearly defined and the outcome is diffused by data scattering. Furthermore, the data indicate *no* saturation of the interface parameter S for $S = 1$. Considering the definition of S, it follows that the true Schottky limit should occur for some number $S \approx 2.0$–3.0 rather than for exactly $S = 1$ as previously claimed.

In 1969, Kurtin *et al.*[1] presented an extensive compilation of experimental metal-semiconductor interface (MSI) data. In classifying the behavior of MSI's the interface slope parameter $S = \partial\Phi_B/\partial X_m$ was used to describe the extent of Fermi-level stabilization for a given semiconductor. Here Φ_B denotes the rectifying barrier height of the MSI and X_m denotes the metal electronegativity. The definition of S as a descriptive interface index is based on a linear interface potential theory developed by Cowley and Sze[2] and by Heine.[3] If correct, this linear theory yields the striking result that the interface behavior of a given semiconductor can be described by a characteristic parameter S independent of the metal with which it is in contact. The theory assumes that a dipole is created at the interface formed by localized states on the semiconductor side, which in turn are more or less filled by electrons spilling over from the metal. Thus, by moving the Fermi level (i.e., changing the metal characterized by its electronegativity X_m) the barrier height is changed at a rate given by S.

Two limiting cases can be considered. The case of complete or nearly complete Fermi-level stabilization ($S \approx 0$) as found in Si or Ge, for example, is attributed to the existence of a high density of interface states in the gap of these semiconductors which "pin" the Fermi level. This limit had been first proposed qualitatively by Bardeen,[4] who related the stabilization to surface states. Later the problem had been formulated more rigorously by Heine,[3] who noted that true surface states should be absent in a metal-semiconductor interface, however, metal states tailing into the semiconductor would play a similar role of Fermi-level stabilization. A number of more-sophisticated calculations of the interface dipole[5-8] as well as theories involving band-narrowing, many-body interactions, and elementary excitation[9,10] confirm the existence of the $S \approx 0$ Bardeen limit.

The opposite limit of little or no Fermi-level stabilization, referred to as the Schottky limit, is reached if virtually no interface states exist in the semiconducting gaps. The important point to note is that the limit (no stabilization) is a $S = A$, where $A \equiv \partial\Phi_m^I/\partial X_m$. The quantity A, which is not in general equal to 1 or may not even be metal independent, relates the metal electronegativity X_m (e.g., on a Pauling scale[11]) to an "internal" metal work function Φ_m^I. The term "internal" emphasizes the difference between Φ_m^I and the usual (measured) metal work function Φ_m which characterizes the metal-vacuum interface and which contains an additional electrostatic contribution D from the metal surface dipole. Even though this latter fact (namely, $\Phi_m = \Phi_m^I + D$) was realized early and led to the use of X_m rather than Φ_m in characterizing the metal,[12] the correct value of $A \neq 1$ was usually omitted.[13] One exception is the theoretical work of Ref. 8, where a value of $A = 2.27$ was used in the calculations. As discussed later, this value though quite different from Ref. 1 may not be completely exact either since it originates from correlating measured work functions Φ_m with electronegativities X_m and thus is affected by the electrostatic surface dipole.

Moreover, in Ref. 1 S values were plotted for a number of semiconductors as a function of their electronegativity difference ΔX in a way which strongly suggested that, for semiconductors with $\Delta X > 1.0$, saturation is reached, i.e., the Schottky limit is reached at $S = 1$, i.e., $A = 1$. This plot, which is reproduced in Fig. 1 also suggested a rather abrupt transition between $S \approx 0$ and $S \approx 1$ around $\Delta X \approx 0.8$, which could not be explained satisfactorily by the calculations of Refs. 5–8. [The data points of SiC and C (diamond) are taken from Ref. 14. The originally published S value for SiC of 0.4 is thus corrected to 0.04.] Instead, many-body effects such as those proposed for electronic states in glasses were invoked to explain the "sudden" transition between covalent ($S \approx 0$) and ionic ($S \approx 1$) regimes.[15]

It is the purpose of this note to show that (a) the data contained a great deal of scattering and if they

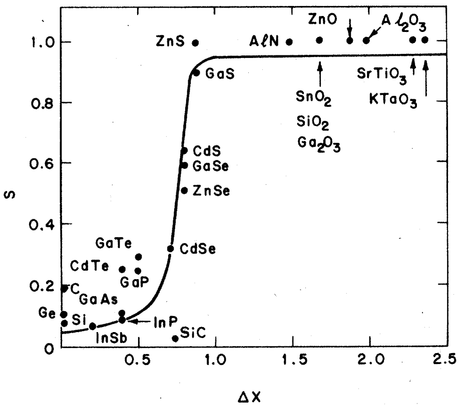

FIG. 1. Original plot of interface slope parameter S versus semiconductor electronegativity difference ΔX as given in Ref. 1.

are least-squares fitted, the suggested "sudden" transition is rather smooth and diffuse. (b) Taking into account the correct definition of S, the Schottky limit is not found for $S=1$ but should rather occur for some value $S \approx 2.0$–3.0. (c) For ionic semiconductors like ZnS, SiO_2, ZnO, SnO_2, Al_2O_3, or $SrTiO_3$ with ΔX ranging between 1.0 and 2.5, this suggested Schottky limit has by far not yet been reached.

As can already be seen from the original data plotted in Fig. 1 of Ref. 1, the scattering of barrier height values Φ_B for a given semiconductor or insulator (like SiO_2) as a function of metal electronegativities is rather high and straight-line fits (whether least squares or not) may become quite questionable in certain cases. The scattering varies from case to case and generally increases with the deduced value of S, i.e., with the ionicity (or band gap) of the semiconducting compound. However, even for a covalent material as Si, significant scattering was reported in the literature.[16] In view of these difficulties, we have reexamined the original data as far as they are available in Refs. 1, 12, 17, and 18 and performed least-squares fits to them. The results (listed in Table I) deviate significantly from those reported in Ref. 1, in some cases by more than 50%. In particular, the newer results for $SrTiO_3$ of Ref. 17 are not at all compatible with the $S=1$ value reported in Ref. 1. Moreover, a χ^2 analysis of the quality of the fits showed that the uncertainty in S is at least ±20% purely on the basis of data statistics. It may thus be still questionable whether the least-squares-fitted values describe the physical situation much better than the values reported in Ref. 1; they have, however, a statistical meaning. The main result is that straight-line fits (i.e., the linear interface theories) only very roughly describe the situation and may contain much arbitrariness like weighting of certain "good quality" metal-semiconductor contacts. The poor quality of the fits also indicates that a number of other effects, such as atomic interdiffusion[10] and formation of interface complexes, are of equal importance.

Bearing in mind these uncertainties, however, one may still attempt to classify MSI's in the spirit of the linear interface theory. Thus, in Figs. 2(a) and 2(b) the least-squares-fitted S values are plotted against the electronegativity difference ΔX and the semiconductor polarizability as proposed in Ref. 10. We used here the total polarizability $\epsilon_0 - 1$ which contains contributions from ion motion, i.e., ion relaxation in the interface region.[19] Though the data show a wide scatter, no saturation in S is obvious. More data of compounds with low polarizabilities would, however, be desirable to establish this point. It should be noted that both features, wide scatter and the absence of any saturation show up equally, whether S is plotted versus ΔX or versus $\epsilon_0 - 1$. However, the $\epsilon_0 - 1$ plot is more consistent with the spirit of the linear interface theory. To distinguish between the validity of ΔX or $\epsilon_0 - 1$ as coordinate, the case of diamond should provide a critical test. The results on diamond reported in Ref. 14 seem to favor the electronegativity coordinate ΔX. However, there is a possibility that graphitelike structures are formed at the C-metal interface, changing the effective polarizability to higher values.

TABLE I. Table of interface slope parameters $S = \partial\Phi_B/\partial X_m$. The quoted experimental values are least-squares fitted to the results of Refs. 1, 12, 14, and 22. Also indicated are theoretical results of Louie, Chelikowsky, and Cohen (LCC) (Ref. 8) using $A=2.86$, and empirical values estimated as described in the text.

	$\Delta S = \pm 20\%$		Present
	expt	LCC	estimate
C (diamond)	0.20		0.45
Si	0.08	0.13	0.16
Ge	0.09		0.13
GaAs	0.15	0.13	0.36
GaP	0.33		0.50
CdTe	0.16		0.56
CdSe	0.18		0.69
CdS	0.70		0.76
GaTe	0.32		
GaSe	0.57		
GaS	0.95		
SnO_2	0.83		
ZnSe	0.66	0.50	0.64
ZnS	1.18	0.88	0.87
ZnO	0.95		0.86
SiO_2	1.52		
$SrTiO_3$	0.45		

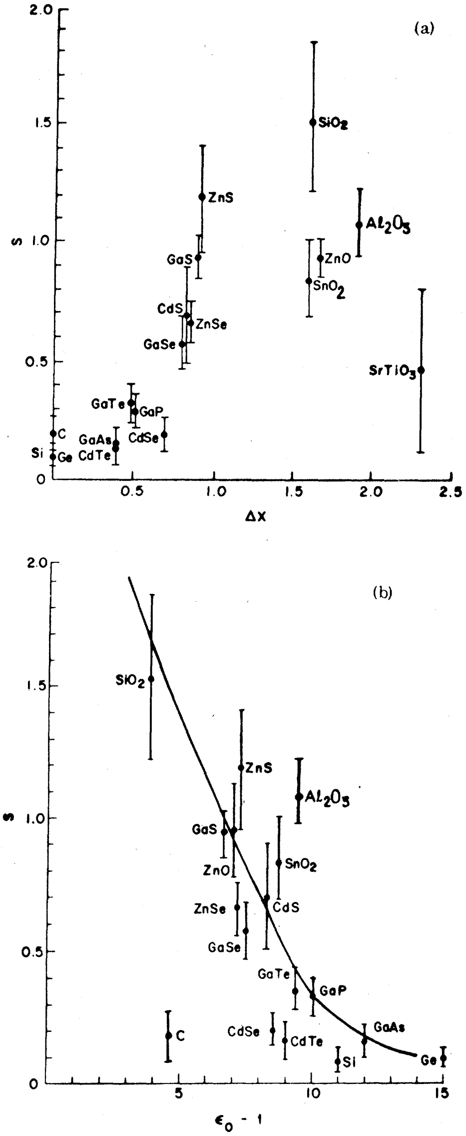

FIG. 2. Least-squares-fitted experimental S parameters plotted (a) vs electronegativity difference ΔX and (b) vs total semiconductor polarizability.

The deviation from general behavior of the two cadmium compounds (CdSe and CdTe) may in fact be due to atomic interdiffusion or cation substitution in the metal-interface region. Evidence for similar anomalies in the CdS_xSe_{1-x} alloy-interface systems have been reported[12] and interpreted in these terms.[10]

We shall now turn to the second problem, the definition of S and its upper saturation limit A. The linear theory predicts saturation at $\partial\Phi_B/\partial\Phi_m^I = 1$ or $S=\partial\Phi_B/\partial X_m = A$. In order to use tabulated metal electronegativities (e.g., Pauling's values[11]), a connection between the internal work function Φ_m^I and the electronegativity X_m has to be established; in other words, an energy scale has to be correlated with X_m. Mulliken[20] first noted that for group-I and group-VII elements the electronegativity X_m should be proportional to the arithmetic mean of the first ionization potential Φ and the electron affinity X:

$$M=\tfrac{1}{2}(\Phi+X)=AX_m, \quad \text{(in eV)}, \tag{1}$$

where M has been called the Mulliken potential[21] and expresses electronegativities in eV. By definition, this potential M may be correlated with the internal work function Φ_m^I. Mulliken's arguments were later extended to all first- and second-row elements and a proportionality factor[22] of $A = 3.15$ was deduced. Using different data, Pauling proposed a factor[11] of $A = 2.71$. A proportionality factor of $A = 2.86$, based on more-recent data, has been used very successfully by Nethercot[21] to predict photoelectric threshold energies for a variety of compound semiconductors.

A correlation of vacuum-metal work functions Φ_m with Pauling electronegativities has been given by Gordy and Thomas[23] and an empirical linear relationship of the form

$$\Phi_m = 2.27X_m + 0.34 \tag{2}$$

has been found. This form is roughly compatible with the values of A given above if one takes into account the wide spread of experimental work-function data. As noted, these are affected by an electrostatic surface dipole which is small for low-density materials such as Cs and which increases with electron density (i.e., increasing X_m) and becomes strongly surface-structure dependent.[18,24] This in fact would suggest that the value of A should be somewhat smaller than 2.27.

All arguments given above suggest that the Schottky limit for MSI behavior is reached at some number $S \approx 2.0-3.0$ which is not clearly defined and not exactly at $S = 1$ as previously proposed. Data on ZnS, ZnO, SnO_2, $SrTiO_3$, Al_2O_3, and SiO_2, previously believed to represent the Schottky limit, are thus far below any limiting value. Thus, we do not expect any saturation at $S = 1$ and in fact do not find any in our least-squares-fitted data. Moreover, calculations based on the linear interface theory[5-8] yield reasonable results of S if proportionality factors of $A \approx 2.0-3.0$ are used (see Table I, in which we used $A = 2.86$ as in Ref. 21).

We have also included in Table I estimated S values for some tetrahedrally coordinated semiconductors, which are empirically derived from dielectric properties using the linear equation[2,3,8]

$$S = A/(1+4\pi e^2 D_s \delta). \tag{3}$$

The interface density of states D_s is interpolated between calculated[8] values for Si, GaAs, ZnSe, and ZnS assuming it to be inversely proportional to the average gap E_g in the semiconductor. The effective penetration depth δ of interface states is estimated to be

$$\delta = t_m/\epsilon_m + t_s/\epsilon_s \,, \tag{4}$$

where $t_m/\epsilon_m \approx 0.5$ Å, a typical (rather constant) screening length in metals and where $t_s \approx 2\sqrt{\Delta}/E_g$, given by an effective semiconductor band width Δ and the average gap E_g.[3] The values of Δ vary from ~13.0 eV for Si to ~6.0 eV for ZnO and are interpolated using the electronegativity difference ΔX. The screening in the semiconductor ϵ_s is composed of a strongly wave-vector-dependent electronic part as described in Refs. 8 and 9 in addition to an ionic lattice part assumed to be wave-vector independent that accounts for atom relaxation effects in the interface. With these input data,[25] D_s and δ decrease from 5×10^{14} states/eV cm^2 and ~2 Å for Si to ~2×10^{14} states/eV cm^2 and ~0.6 Å for ZnO, respectively. As can be seen from Table I, this very crude model yields reasonable S values for most of the semiconductors with uncertainties comparable to the experimental errors.

We find from this analysis that the original MSI data show an enormous amount of scattering and that straight-line fits yielding the interface index S are rather uncertain. No saturation at $S=1$ is found if the data are least-squares fitted. This also is theoretically unexpected since S is defined with respect to the metal electronegativity and not with respect to an *internal* work function. Theoretical considerations rather suggest some limiting value of S between 2.0 and 3.0, which may not clearly be defined.

The linear one-electron MSI theory, while not expected to be quantitative, yeilds reasonable answers for MSI behavior in *qualitative* agreement with experiment, if one keeps in mind the uncertainties in experiment and data analysis. More systematic experimental results are clearly needed before conclusions as to the range of validity of this theory can be drawn, in particular to decide on the appropriateness whether to use the electronegativity difference or the polarizability as a characteristic coordinate.

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