

SCHOTTKY BARRIER HEIGHTS: ARE THEY REALLY CORRELATED WITH ANY OTHER PARAMETER?

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A subject of recent discussion in the literature concerns the role of interface chemical reactivity in the determination of the Schottky barrier height.

In the work reported in this paper we sought possible correlations between the macroscopic interface dipole, the metal work function and the metal–semiconductor reactivity. Experimental results for Schottky barriers on clean cleaved ZnS, CdS and GaP and on chemically etched InP are discussed in detail.

One result that we did find was that, in all the cases considered, the macroscopic interface dipole does not depend on the degree of metal–semiconductor reactivity.

Although great progress has been made in the understanding of the physical and chemical mechanisms of Schottky barrier formation, this problem is still a matter of controversy. The best illustration of its complexity is the large number of models formulated to describe the properties of the metal–semiconductor junction (for a review see for example refs. 1–3).

Recently it has been established that chemical reactions and interdiffusion can take place at metal–semiconductor interfaces, even at room temperature (see for example refs. 4–8).

A correlation between the barrier height and the metal–semiconductor heats of reaction has been proposed by Brillson^{5,8}. However, in spite of possible metal–semiconductor interactions and interdiffusion, the barrier heights observed by Spicer *et al.*^{9,10} for III–V compound semiconductors are almost the same for a wide range of metals. Furthermore, it has not been resolved whether chemical processes, if really important, influence the semiconductor surface region (*e.g.* by the formation of interface traps) or whether (as proposed by Brillson¹¹) they are directly responsible for the formation of an interface dipole through chemical bonding between the metal and the semiconductor. In the first case the fixation of the barrier height is the prerequisite to the dipole formation, and vice versa in the second case.

In the work reported in this paper we looked, in particular, for possible correlations between the macroscopic interface dipole, the metal work function, and the metal–semiconductor heat of reaction on compound semiconductors.

The interface dipole is defined as follows:

$$\phi_{\text{dip}} = \phi_{\text{m}} - \chi - \phi_{\text{bn}} \quad (1)$$

where ϕ_m is the metal work function, χ is the electron affinity of the clean semiconductor surface and ϕ_{bn} is the surface barrier height (Fig. 1). It should be noted that, unlike Brillson¹¹, we do not include the contribution of ϕ_{dip} in the magnitude of the surface barrier height.

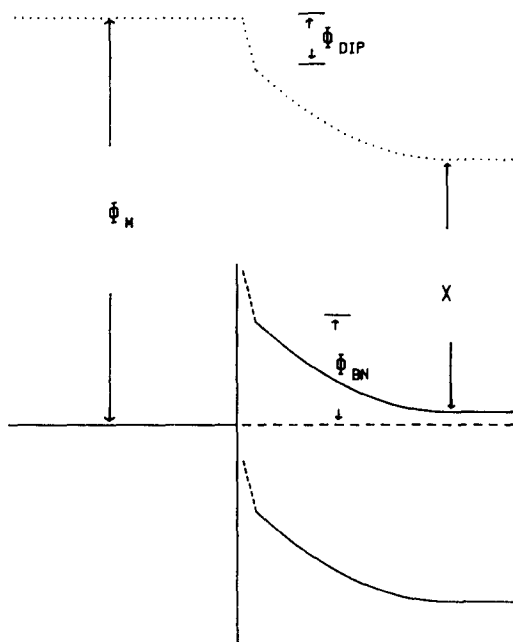


Fig. 1. Energy band diagram of metal–semiconductor (n type) contacts.

The value of ϕ_{bn} corresponds to the surface barrier height commonly measured by electric and photoelectric methods^{1,2}. The interface dipole can be due to local charge rearrangement (1–10 Å range) in the metal–semiconductor interface³. For example, in the model of Bardeen¹², ϕ_{dip} is the potential drop across the ultrathin insulating interfacial layer. In models which take into account possible interface traps and charge penetration into the semiconductor interface region, ϕ_{dip} is the potential drop across the perturbed semiconductor surface layer (see for example refs. 13–16). The interface dipole can also be affected by local chemical bonding between the metal and the semiconductor as well as by modifications of ϕ_m and χ due to metal–semiconductor interdiffusion.

For the discussion presented here we utilize data available in the literature^{17,18}. For ZnS, CdS and GaP the Schottky contacts were formed on semiconductors cleaved in vacuum, and the barrier heights were measured by internal photoemission¹⁷. For InP the contacts were formed on a chemically etched surface, and the barrier heights were determined from forward bias current–voltage characteristics¹⁸. In all cases, sufficiently thick metal overlayers were used to stabilize the metal work function.

Figure 2 shows the magnitude of the interface dipoles *versus* the measured surface barrier height for various metals on ZnS, CdS, GaP and InP. The magnitudes of the interface dipoles were calculated from eqn. (1) with metal work

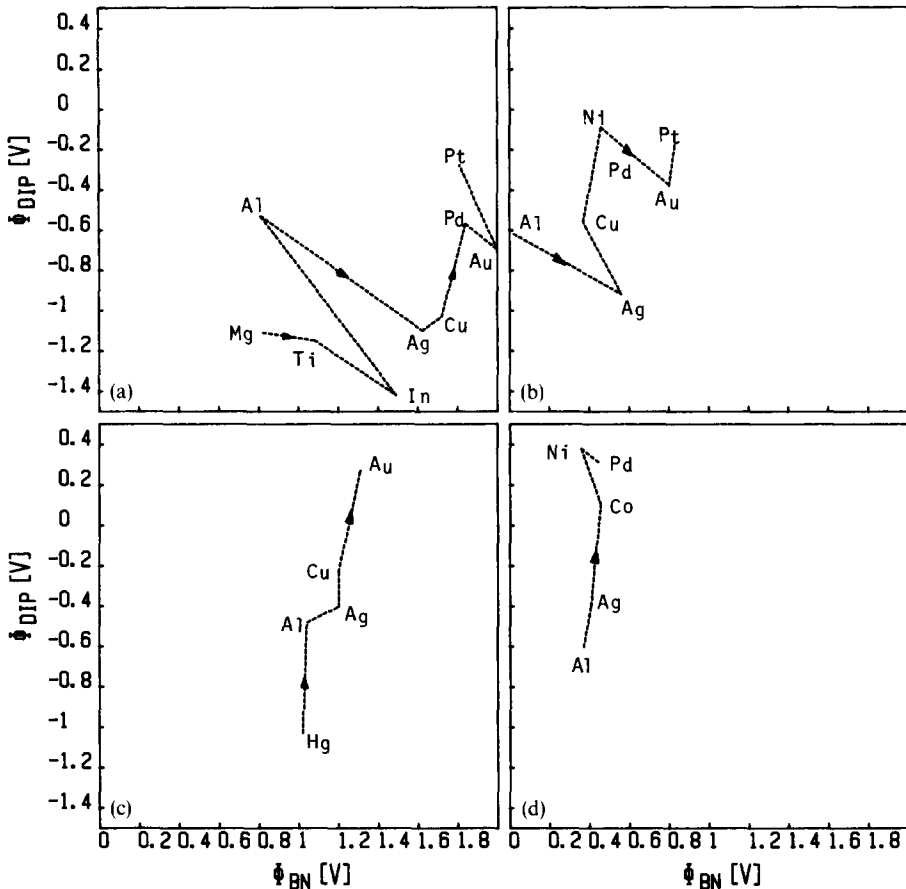


Fig. 2. Magnitude of the interface dipole vs. the measured surface barrier height for various metals on (a) ZnS, (b) CdS, (c) GaP and (d) InP. The direction of increasing metal work function is indicated by arrows on the broken curves.

functions taken from ref. 1, Table 2.1, and semiconductor electron affinities taken from ref. 19. It should be noted that it is not relevant to our argument to know the accurate value of χ , since we are concerned only with changes in interface dipoles as a function of the metal overlayer.

The direction of increasing metal work function is indicated by arrows on the broken curve in Fig. 2.

The range of (available) ϕ_{bn} values is considerably wider for ionic semiconductors (ZnS and CdS) than for covalent semiconductors (GaP and InP). For all the semiconductors under consideration the ranges of ϕ_{dip} are similar.

The small range of surface barrier heights for covalent semiconductors strongly support the model of Spicer *et al.*^{9,10} of metal-induced but metal-independent interface traps. In this "unified model" the adatoms disturb the semiconductor surface indirectly by forming defect levels, such as anion vacancies²⁰⁻²³ and/or antisite defects²⁴.

It should be pointed out that the observation of a nearly monotonic ϕ_{dip} versus

ϕ_m relation for covalent semiconductors (see Fig. 2 where the arrows indicate the direction of increasing ϕ_m) also indicates that the energetic distribution of interface traps is essentially independent of the metal, which constitutes additional support for the model of Spicer *et al.*

In contrast, the non-monotonic ϕ_{dip} versus ϕ_m and ϕ_{dip} versus ϕ_{bn} relations, which are particularly apparent for ionic semiconductors (Fig. 2), cannot be explained on the basis of models in which specific effects of the deposited metals on the interface properties are neglected.

If it is assumed that interface traps (intrinsic and/or metal induced) are responsible for Fermi level pinning and dipole formation, the metal-independent traps dominate at metal-covalent semiconductor interfaces and the metal-dependent traps (with different "neutral levels") at metal-ionic semiconductor interfaces.

For covalent semiconductors the adatoms induce interface traps which are the result of structural defects in the semiconductor lattice produced by the perturbation due to adatoms on the surface. The same atoms cannot induce similar structural

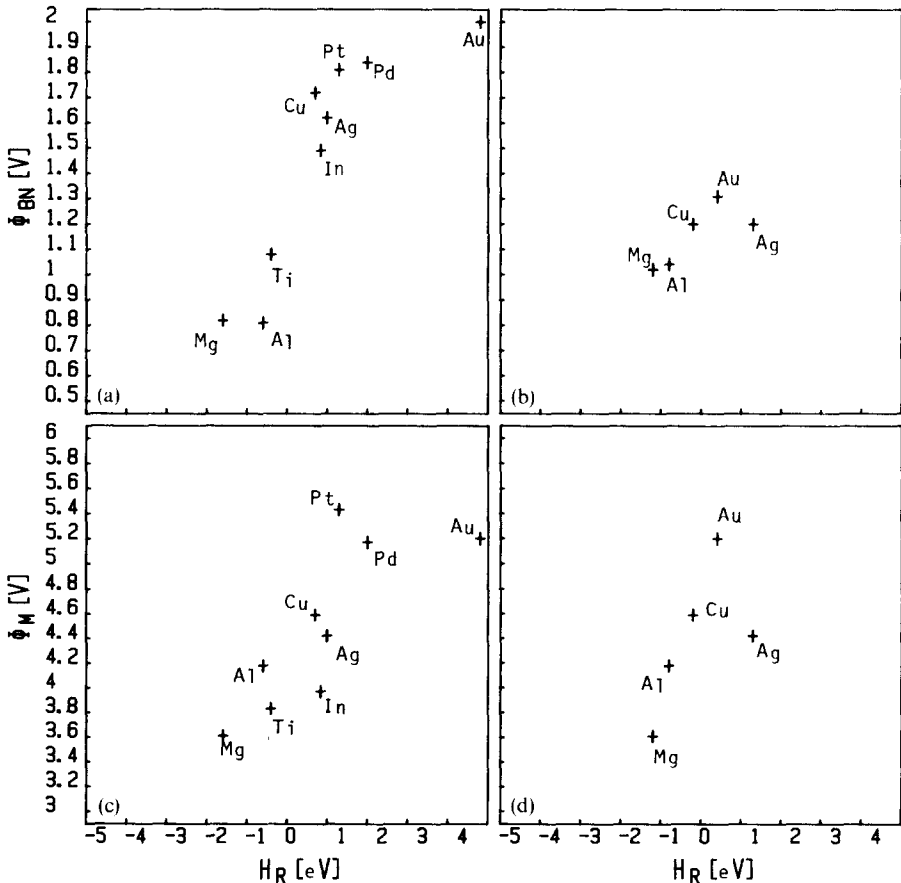


Fig. 3. Magnitude of the surface barrier height ϕ_{bn} vs. the heat of reaction H_R and, for comparison, ϕ_m vs. H_R , for (a), (c) ZnS and (b), (d) GaP. The H_R data are taken from ref. 5, Fig. 3.

defects on the surface of ionic semiconductors because of the stronger bonding between the atoms of the semiconductor. Consequently the extrinsic metal-dependent interface traps due to the presence of metal adatoms on the semiconductor surface are relatively more important for ionic semiconductors.

On the basis of Fig. 2 it is also clear that the Schottky limit²⁵ is far from being attained in all the cases under consideration, including ionic semiconductors. In addition, the application of the linear theory with the "interface behaviour index" S ²⁶ is seriously hampered by the strongly non-monotonic behaviour of ϕ_{dip} versus ϕ_{m} observed for ionic semiconductors as mentioned above. Consequently the abrupt transition in S considered as a universal change-over from covalent to ionic semiconductors²⁶ is questionable, as was also pointed out by Schluter²⁷.

By plotting the barrier heights ϕ_{bn} against the metal-semiconductor heat of reaction, Brillson⁵, Williams *et al.*²⁸ and Hokelek and Robinson¹⁸ have obtained an S-type curve; this result is commonly attributed to a strong correlation between the barrier height and the chemical reactivity.

Such correlation, however, should be handled with caution. Figure 3 shows

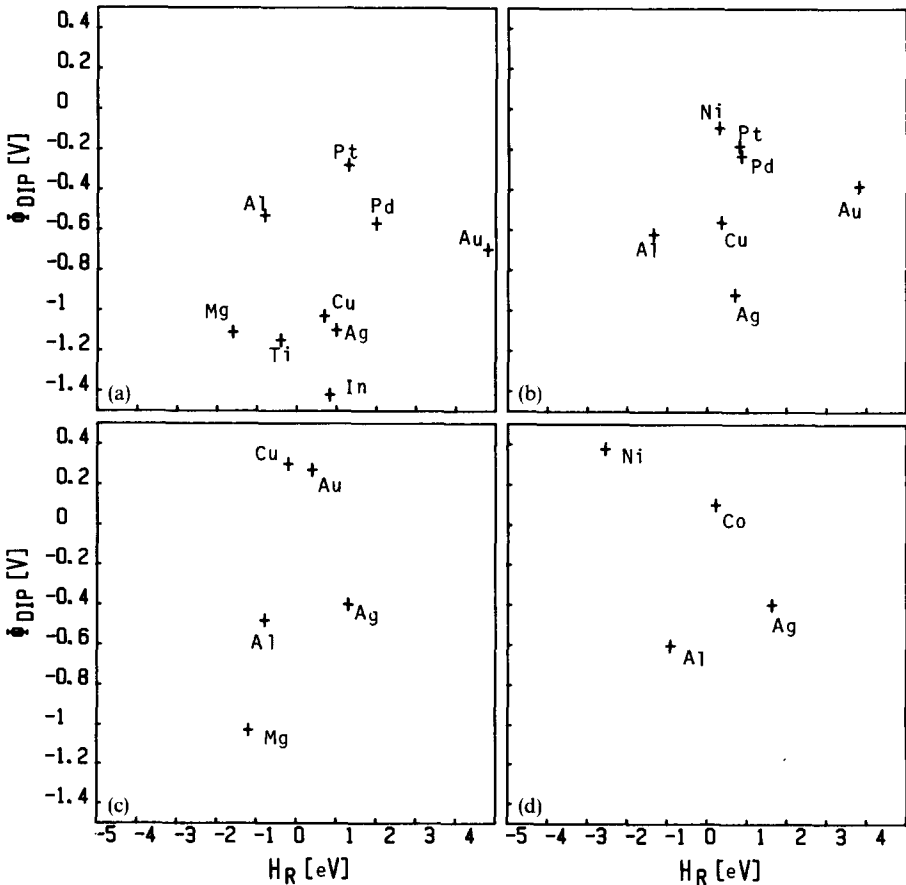


Fig. 4. Magnitude of the interface dipole vs. the metal-semiconductor heat of reaction for (a) ZnS, (b) CdS, (c) GaP and (d) InP.

plots of ϕ_{bn} versus H_{R} and, for comparison, plots of ϕ_{m} versus H_{R} for ZnS and GaP. The two types of diagram are quite similar. Usually more reactive metals (lower H_{R}) have a lower electronegativity and a lower work function ϕ_{m} . Such properties seem to be quite general, in spite of the semiconductor-dependent position of a given metal along the H_{R} axis. Thus the apparent correlation between ϕ_{bn} and H_{R} may simply be a consequence of the real correlation between ϕ_{m} and H_{R} . A similar behaviour is observed for CdS and InP.

In Fig. 4, diagrams of ϕ_{dip} versus H_{R} are shown for ZnS, CdS, GaP and InP. In no case can a correlation between ϕ_{dip} and H_{R} be found. This behaviour indicates that metal–semiconductor interface reactions are not important for the determination of the dipole. The contribution of metal–semiconductor bonding to the interface dipole is masked by the effect of charge redistribution between the metal and the interface traps, probably distributed in the semiconductor surface region to a depth of 2–10 Å. A correlation between the energetic and spatial distribution of the interface traps and the degree of metal–semiconductor chemical reactivity may exist^{8,16} but it is not clear at present.

REFERENCES

- 1 E. H. Rhoderick, *Metal–Semiconductor Contacts*, Clarendon, Oxford, 1978.
- 2 S. M. Sze, *Physics of Semiconductor Devices*, Wiley, New York, 1981.
- 3 M. Schluter, *Thin Solid Films*, **93** (1982) 3.
- 4 L. J. Brillson, *Phys. Rev. B*, **18** (1978) 2341.
- 5 L. J. Brillson, *Phys. Rev. Lett.*, **40** (1978) 260.
- 6 P. W. Chye, I. Lindau, P. Pianetta, C. M. Garner and W. E. Spicer, *Phys. Rev. B*, **17** (1978) 2682.
- 7 L. J. Brillson, C. F. Brucker, A. D. Katnani, N. G. Stoffel and G. Margitondo, *Appl. Phys. Lett.*, **38** (1981) 784.
- 8 L. J. Brillson, *Thin Solid Films*, **89** (1982) 461.
- 9 W. E. Spicer, P. W. Chye, P. R. Skeath, C. Y. Su and I. Lindau, *J. Vac. Sci. Technol.*, **16** (1979) 1422.
- 10 W. E. Spicer, S. Eglash, I. Lindau, C. Y. Su and P. Skeath, *Thin Solid Films*, **89** (1982) 447.
- 11 L. J. Brillson, *J. Vac. Sci. Technol.*, **16** (1979) 1137.
- 12 J. Bardeen, *Phys. Rev.*, **71** (1947) 717.
- 13 V. Heine, *Phys. Rev. A*, **138** (1965) 1689.
- 14 A. M. Cowley and S. M. Sze, *J. Appl. Phys.*, **36** (1965) 3212.
- 15 S. G. Louie, J. R. Chelikowsky and M. L. Cohen, *J. Vac. Sci. Technol.*, **13** (1976) 790.
- 16 S. Krawczyk and P. Viktorovitch, to be published.
- 17 C. A. Mead, *Solid-State Electron.*, **9** (1966) 1023.
- 18 E. Hokelek and G. Y. Robinson, *Appl. Phys. Lett.*, **40** (1982) 426.
- 19 J. L. Freeouf and J. M. Woodall, *Appl. Phys. Lett.*, **39** (1981) 727.
- 20 M. S. Daw and D. L. Smith, *Phys. Rev. B*, **20** (1979) 5150.
- 21 M. S. Daw and D. L. Smith, *Appl. Phys. Lett.*, **36** (1980) 690.
- 22 M. S. Daw and D. L. Smith, *J. Vac. Sci. Technol.*, **19** (1981) 508.
- 23 H. H. Wieder, *Appl. Phys. Lett.*, **38** (1981) 170.
- 24 R. E. Allen and J. D. Dow, *Phys. Rev. B*, **25** (1982) 1425.
- 25 W. Schottky, *Phys. Z.*, **41** (1940) 570.
- 26 S. Kurtin, T. C. McGill and C. A. Mead, *Phys. Rev. Lett.*, **22** (1969) 1433.
- 27 M. Schluter, *Phys. Rev. B*, **17** (1978) 5044.
- 28 R. H. Williams, R. R. Varma and V. Montgomery, *J. Vac. Sci. Technol.*, **16** (1979) 1418.