

Elementary Excitations at Metal-Semiconductor Interfaces

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A microscopic theory of barrier heights at metal-semiconductor interfaces is proposed. The theory explains the resonance in barrier adjustability as a function of semiconductor ionicity described by Mead *et al.*, in terms of the interfacial-surface plasmon energy and the covalent-bond energy of the semiconductor.

WHEN a metal is brought into contact with a semiconductor, the interfacial region is found to exhibit rectifying properties. The origin of these properties is the accumulation of an excess of electronic charge at the interface. The excess charge creates a potential barrier ϕ_B which can be determined from C - V , I - V and photoresponse measurements.¹

The microscopic nature of the potential barrier has been discussed by several authors. Qualitatively speaking, the work function $\phi_{m'}$ of a metal arises because of the spreading out of electronic charge by a fraction of an angstrom into vacuum. Suppose that, following Schottky,² we ascribe the same origin to the work function ϕ_s of the semiconductor, and assume that the interface is ideal³ and that the charge in the interfacial region can be obtained by superposition of the spread-out charges of the metal and semiconductor. Then the barrier height ϕ_B is given by²

$$\phi_B = \phi_{m'} - \phi_s. \quad (1)$$

One may also treat the interface as intermetallic but abandon the approximation of superposed charge densities, instead relying on wave-function matching. Then (1) is no longer required to hold.⁴

Bardeen has given⁵ a qualitative discussion of the interfacial region in terms of the dielectric double layer generated by mismatch between metallic and covalent properties. He was particularly concerned to explain the observation that when the semiconductor was Si or Ge one found that ϕ_B was virtually independent of $\phi_{m'}$, contrary to (1). His explanation utilized the fact that at the interface one could expect to find surface states, whose filling or emptying could stabilize (or "pin") the barrier height at a nearly constant value. Thus one would have [in place of (1)] the general linear relation

$$\phi_B = S(s)[\phi_{m'} - \phi_s] + \phi_{Be}(s), \quad (2)$$

with $S(\text{Si}) \approx S(\text{Ge}) \approx 0$. Here ϕ_{Be} is a small, nearly constant term associated with elastic mismatch.

A number of workers have stressed that for different materials $0 < S(s) < 1$. In particular, it has been shown by Kurtin, McGill, and Mead⁶ that values of S can be

correlated with the electronegativity difference ΔX between the elements forming binary semiconductors. In order to explain this result using Bardeen's model it appears necessary to carry out elaborate calculations⁷ of the energy levels and dipole moments of surface states as a function of surface charge density. In this paper we show that this is not the case. Indeed, the observed behavior of $S(s)$ can be explained entirely in terms of resonant elementary excitations of the semiconductor and the interface, without invoking knowledge of one-electron surface states.

Charge-density waves in solids are excited at the plasma frequency ω_p , where $\epsilon_1(\omega_p) = 0$ and $\epsilon_1(\omega)$ is the real part of the dispersive dielectric function. Suppose, first, that a binary semiconductor MX is covered by one or two layers of oxide MO or $M'O$. Accumulation of charge at the surface when the contact potential is abruptly "turned on" can be described by excitation of surface plasmons of frequency ω_s . If we denote the real part of the dielectric function of the oxide by $\tilde{\epsilon}_1(\omega)$, we have⁸

$$\epsilon_1(\omega_s) + \tilde{\epsilon}_1(\omega_s) = 0. \quad (3)$$

In order for the surface plasmons at the MX - MO interface to be stable, it is necessary that $\hbar\omega_s$ be smaller than the average energy $E_g(MX)$ required to break a covalent bond in the MX crystal. For tetrahedrally coordinated semiconductors of the diamond, zincblende, and wurtzite crystal types, values of E_g have been tabulated.⁹ They satisfy the relation

$$\epsilon_1^{MX}(\omega) = 1 + \frac{(\hbar\omega_p)^2}{E_g^2 - (\hbar\omega)^2} D_{MX}, \quad (4)$$

where $\omega_p^2 = 4\pi N e^2 / m$, $N = 4/\text{atomic volume}$, and D_{MX} is a correction factor which allows for the polarization of d core levels.

In general, we expect that the frequency-dependent polarizability of the MO oxide will be less than that of the MX semiconductor. Then (3) and (4) imply that ω_s lies in the "pass band"

$$\omega_g(MX) < \omega_s < \tilde{\omega}_g(MO) \quad (\text{Bardeen}), \quad (5)$$

¹ C. R. Crowell, *Surface Sci.* **13**, 13 (1969).

² W. Schottky, *Z. Physik* **118**, 539 (1942).

³ By an ideal interface we mean one which is free of contamination and which separates two periodic semi-infinite crystals.

⁴ V. Heine, *Phys. Rev.* **138**, A1689 (1965).

⁵ J. Bardeen, *Phys. Rev.* **71**, 717 (1947).

⁶ S. Kurtin, T. C. McGill, and C. A. Mead, *Phys. Rev. Letters* **22**, 992 (1968).

⁷ R. O. Jones, *Phys. Rev. Letters* **20**, 992 (1968). Jones has treated ideal semiconductor surface states using a realistic band model, but his calculation makes no allowance for the fact that the energy of each surface state depends on the surface charge. His calculation also says nothing about surface dipole moments.

⁸ F. A. Stern and R. A. Ferrell, *Phys. Rev.* **120**, 130 (1960).

⁹ J. C. Phillips, *Phys. Rev. Letters* **20**, 550 (1968); **22**, 285 (1968); J. A. Van Vechten, *Phys. Rev.* (to be published).

TABLE I. Some representative values of dielectric constants of MX semiconductors and their cation oxides, largely taken from Ref. 9. It should be borne in mind that $\epsilon(MO)$ represents only an estimate of the dielectric properties of the interfacial region, inasmuch as the latter is not crystalline and probably not homogeneous. If one estimates that $\epsilon(\text{Ga}_2\text{O}_3) = \epsilon(\text{Al}_2\text{O}_3)[\epsilon(\text{GeO}_2)/\epsilon(\text{SiO}_2)]$ one obtains $\epsilon(\text{Ga}_2\text{O}_3) = 4.3$. This bears much the same relation to $\epsilon(\text{GaSe})$ as $\epsilon(\text{CdS})$ and $\epsilon(\text{CdSe})$ do to $\epsilon(\text{CdO})$, suggesting that GaSe also belongs in the transition region described by Eq. (7).

MX	$\epsilon(MX)$	MO	$\epsilon(MO)$
Si	12.0	SiO_2	4.3
Ge	16.0	GeO_2	6.0
AlAs	10.3	Al_2O_3	3.1
GaSe	4.7 ^a
CdTe	7.2	CdO	5.0
CdSe	5.8	CdO	5.0
CdS	5.2	CdO	5.0
ZnSe	5.9	ZnO	4.0
ZnS	5.2	ZnO	4.0

^a R. H. Bube and E. L. Lind, Phys. Rev. **115**, 1164 (1959).

where ω_g and $\tilde{\omega}_g$ are the average gap frequencies of MX and MO , respectively. According to (5), the Bardeen limit [$S(s) \ll 1$] is satisfied because $\omega_s > \omega_g$, so that charge does not accumulate at the semiconductor side of the interface.

Another possibility is that the semiconductor is of the large-gap or ionic type, and that the oxide forms with the metal M' , i.e., we have an $M'O$ oxide. In this case the polarizability of the $M'O$ interface will be greater than that of the MX semiconductor or insulator. Then (3) and (4) imply

$$\tilde{\omega}_g(M'O) < \omega_s < \omega_g(MX) \quad (\text{Schottky}). \quad (6)$$

Finally, one has the possibility of a narrow transition region

$$\omega_g(MX) \approx \tilde{\omega}_g(MO) \approx \tilde{\omega}_g(M'O) \quad (7)$$

that appears to hold⁶ for Cd salts and layer semiconductors such as GaSe.

If a stream of metal atoms has been deposited in high vacuum on a freshly cleaved semiconductor, there may be little or no oxide present. Our theory then requires that the $M'X$ bonds have lower polarizability than the MX bonds. Because binary polarizabilities generally decrease with increasing electronegativity difference, such is expected to be the case. In general, one would also expect the interface to be characterized by lower valence electron density. This effectively decreases the interfacial polarizability, leading to the Bardeen limit (5). In cases where an oxide monolayer or two is actually present, so that the dielectric properties of the interface can be estimated, one can compare the dielectric constants of Ge, Si, AlAs with GeO_2 , SiO_2 , Al_2O_3 in Table I. Clearly, these crystals fall in the Bardeen limit (5). On the other hand, the dielectric constants of CdTe, CdSe, and CdS approach those of CdO, which explains why these crystals belong to the transition region (7). At truly intermetallic interfaces, almost no

charge accumulation is expected, i.e., $\phi_B = \phi_{Be}$. This is found to be the case for PtSi-Si interfaces.¹⁰

It may be helpful to visualize what happens to the interfacial region as intimate contact is made between the semiconductor and metal. Suppose that the system, metal M' -monolayer O-semiconductor MX , goes through three stages. For $t < 0$ the work functions of M' , $M'O$, MO , and MX are all taken to be the same. At $t = 0$ the actual work functions are "turned on." The response of the system at times $t > 0$ is divided into two parts, $0 < t < t_1$ and $t > t_1$. Here t_1 is a time such that

$$\hbar/E_g \ll t_1 \ll 1/\omega_D, \quad (8)$$

where E_g and ω_D are the average energy gap and the Debye frequency of $M'O$, MO , or MX .

The response of the valence electrons is sketched in Fig. 1. In Fig. 1(a) we have the situation where the work functions are all the same. Because there is no contact potential difference, there is little tendency for valence electrons to accumulate near the interface, and we have

$$\phi_B = \phi_{Be} \approx 0. \quad (9)$$

At $t = 0$ the work function difference $\Delta\phi = \phi_{m'} - \phi_s$ is turned on. This is divided into two parts, $a\Delta\phi$ being added to ϕ_B and $(1-a)\Delta\phi$ appearing as a potential drop across the oxide. The charge that accumulates near the interface is the nonlinear surface plasmon response to the turning on of the contact potential differences $\phi_{m'} - \phi_0$ and $\phi_0 - \phi_s$, where ϕ_0 is the work function of the oxide.

During the interval $0 < t \ll t_1$ shown in Fig. 1(b), neither the semiconductor nor the oxide ions have time

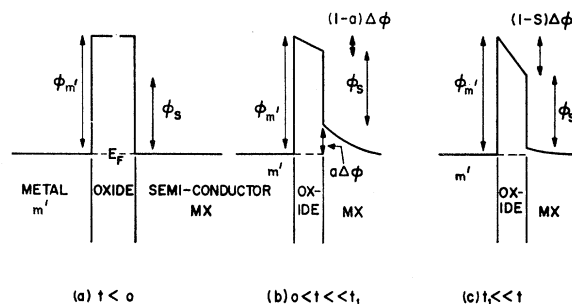


FIG. 1. Response of the potential near the interface between a metal M' and a covalent semiconductor MX in the Bardeen limit [$S(s) \ll 1$] as contact potential differences are turned on. In (a) all work functions are the same (contact potential difference turned off). In (b) $\Delta\phi = \phi_{M'} - \phi_s$ has been turned on, but so short a time has elapsed that only the valence electrons (not the ions) have responded to the difference. In (c) the actual situation, including the effects of ion deformation, is shown. The barrier height is small. In the Schottky or ionic limit, the oxide deforms and almost all the potential drop occurs in the semiconductor.

¹⁰ M. P. Lepselter and S. M. Sze, Bell System Tech. J. **47**, 195 (1968). Information on ϵ_1 for PtSi [C. T. Neppel and J. H. Wernick (to be published)] suggests that $\epsilon_1(\omega) < 0$ for $\hbar\omega < 5$ eV, thus placing the PtSi-Si interface in the extreme Bardeen (almost Ohmic) limit, as observed.

to respond to the forces exerted on them. By phase-space considerations (very thin oxide), $a \approx 1$, and during this interval the Schottky relation (1) holds approximately.

What happens now for $t \gg t_1$ [Fig. 1(c)] depends on the relative lattice rigidities of the oxide and the semiconductor. Again $\Delta\phi$ is separated into two parts, $S\Delta\phi$ being added to ϕ_B and $(1-S)\Delta\phi$ being described by an oxide dielectric double layer. If the oxide is more stable [as is the case when $\omega_g(MX) < \omega_s < \tilde{\omega}_g(MO)$ described by Eq. (5)], near the interface the semiconductor ions will be displaced quasielastically in such a way as to eject the accumulated charge described by surface plasmons into the oxide. This gives the Bardeen limit $S(s) \approx 0$. On the other hand, if the semiconductor is so ionic itself as to be more stable than the $M'O$ oxide, then the latter ejects its share of the interfacial charge into the semiconductor, and the Schottky limit $S(s) \approx 1$ holds. The deformation mechanism proposed here is

¹¹ J. C. Phillips, Phys. Rev. Letters **22**, 285 (1969).

related to the cancellation theorem¹¹ for substitutional isoelectronic impurities, where a similar charge accumulation and ejection occurs because of electronegativity differences.

Because of the quasielastic deformation associated with charge ejection in the Bardeen limit, the mathematics of surface states at ideal interfaces⁷ may not be quite relevant to barrier heights in this limit. There one would expect elastic mismatch to account for the small barrier heights (of order a few tenths of an eV) that are actually observed. Because lattice distortions are of longer range, one might expect that for a family of elastically similar semiconductors the resulting barrier could be related to properties of the valence and conduction band edges only (rather than the average gap E_g). Thus it is not surprising that for many covalent semiconductors¹² (Bardeen limit) $\phi_B \approx \phi_{Be} \approx 0.3\Delta E_{cv}$, where ΔE_{cv} denotes the minimum (direct or indirect) gap between valence- and conduction-band edges.

¹² C. A. Mead and W. G. Spitzer, Phys. Rev. **134**, A173 (1964).

Lattice Dynamics of Wurtzite: CdS. II[†]

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A new model for the lattice dynamics of semi-ionic compounds is presented and applied to the computation of phonon dispersion in CdS. The calculated two-phonon density of states as a function of frequency is in agreement with measured infrared absorption in the two-phonon region. Improved values of the microscopic dielectric, elastic, and piezoelectric coefficients result from a self-consistent least-squares fit of model parameters. The model includes valence-band forces, rigid-ion Coulomb forces, and electronic and ionic polarization; it may be generally applicable to other semi-ionic II-VI compounds.

I. INTRODUCTION

THE present paper reports on an improved model developed for the lattice dynamics of II-VI partially ionic compounds. The improved model is based upon the mixed valence-Coulomb force field model previously used¹ to calculate phonon dispersion in CdS; however, the ionic polarization and the ion deformation

(electronic polarizabilities) are now included in the model, which thereby incorporates most of the likely important basic physical phenomena involved.

As previously noted,¹ only indirect checks of the calculated CdS phonon frequencies are possible, since no experimental inelastic neutron scattering spectra have been reported in CdS from which the dispersion curves can be obtained. We find improved agreement of calculated two-phonon density of modes and two-phonon infrared absorption spectra in the spectral region 400 to 600 cm^{-1} ; major features agree to within 5 cm^{-1} . The elastic and piezoelectric constants of CdS have also been calculated, and the difference with ex-

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¹ M. A. Nusimovici and J. L. Birman, Phys. Rev. **156**, 925 (1967).