which leads to a coupling parameter comparable to (1) provided $q^2/k_s^2 < 1/\epsilon_0$. Again, the detailed analysis of this case remains to be carried out. In a degenerate semiconductor with a large value of $\epsilon_0$ (>10) it appears that the attractive interaction might be strong enough to permit a plasmon bound state or resonance. In this case the resonance could not be observed in electron scattering but might be observable from light scattering experiments or in optical absorption.

The plasmon interaction with the screening clouds surrounding the electrons again is seen to lead to important cancellations. We conclude that, at least for $r_s < 1$, plasmons are nearly independent excitations of an electron gas with a weak attractive interaction. The challenge which remains is to extend these calculations beyond lowest-order terms in $r_s$ to encompass the regime of physical densities.

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# Transition in Schottky Barrier Formation with Chemical Reactivity

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Low-energy electron-loss spectra reveal that a majority of common metals react with CdS, CdSe, and most other covalent semiconductors. Furthermore, barrier heights of metals on individual compound semiconductors exhibit a sharp transition as a function of heat of reaction, increasing dramatically above an experimentally determined critical heat of reaction.

The mechanism of Schottky barrier (SB) formation at metal-semiconductor (M-SC) contacts has been the subject of long-standing controversy. Until recently, the phenomenon of Fermi level pinning associated with interface band bending was thought to be associated with intrinsic surface states of the semiconductor.[1] However, studies of the microscopic II-VI compound semiconductor interfaces by ultrahigh vacuum techniques demonstrate that extrinsic phenomena due to the presence of the deposited metals dominate the SB formation. In particular, reactive metals on these semiconductors form interface compounds,[2] whereas unreactive metals induce new interface states within the band gap.[3] For all metals, dipole layers form which account for the observed electrical behavior of the contact.[4] In this Letter, I present evidence to show that the chemical reactivity of the constituents at a M-SC interface play a central role in determining the SB heights. Kurtin, McGill, and Mead[5] (KMM) have described a fundamental transition in interface behavior related to electronegativity difference of the semiconductor constituents and thereby the degree of lattice ionicity. In turn, this was related to intrinsic surface states via the discontinuity in lattice potential at the surface of covalent versus ionic semiconductors.[6,1] However, this transition can be described equally well in terms of chemical reactivity. Furthermore, the Sb heights of metals on individual semiconductors display a striking correlation with chemical reactivity, exhibiting a sharp transition as a function of heat of reaction $\Delta H_R$ at a critical value determined from low-energy electron-loss spectroscopy (ELS). These results emphasize the importance of local charge redistribution associated with interface chemical reactions rather than with intrinsic surface states of the semiconductor.

Figure 1 illustrates the parameter of interface behavior $S$ for various semiconductors, where $S$ is defined by[5] $qV_B = S(\varphi_M - \varphi_{SC}) + C$. Here $qV_B$, $\varphi_M$, and $\varphi_{SC}$ are the band bending, metal work function, and semiconductor work function, respectively, and $C$ is a constant. The same $S$ values used by KMM are represented here. However, the abscissa of this curve is heat of formation $\Delta H_f$ rather than electronegativity difference $\Delta X$. The smooth curve fitted to the data points is *identical* to that in the $S$ vs $\Delta X$ curve of KMM. This correlation shows that $\Delta H_f$ (and thereby $\Delta H_R$) describe the transition in $S$ at least as well as $\Delta X$. Figure 1 shows that covalent semiconductors have lower $\Delta H_f$ than ionic semiconductors and thus are more likely to react with metals at M-SC interfaces. While $\Delta H_f$ and $\Delta X$ can be related,[7] the chemical heats alone emphasize the microscopic interface's role in determining SB heights.

Figure 1 also shows the representative nature of CdS and CdSe metal interfaces.[6] The wide span of interface behavior between these two systems suggests that their electronic and chemical properties are characteristic of M-SC interfaces in general. ELS measurements of metals on CdS and CdSe reveal the presence of chemically reacted interface layers. For such interfaces, new ELS excitation features appear which are not due to the bulk semiconductor or metal. For Al on CdS and CdSe, these features have been related to coupled interface plasmon modes of the reached interface layer and surrounding media.[2] For unreactive interfaces such as Au on CdSe,[4] only a superposition of ELS features from the semiconductor and metal appear. This contrast between reactive and unreactive interfaces is evident for increasing overlayer thicknesses of Cu vs Ag on CdS(10$\bar{1}$0) as shown in Fig. 2. These spectra were obtained with a cylindrical mirror analyzer (CMA) and a glancing incidence electron gun. Incident beam energy was 100 eV and instrumental resolution was 0.7 eV. The ultrahigh vacuum apparatus has been described elsewhere.[8]

The ELS features observed for the cleaved CdS(10$\bar{1}$0) surfaces correspond to bulk and surface plasmons $\omega_p$ and $\omega_{SP}$, a Cd $4d$ level transition to the conduction band, and interband transitions labeled $I_1$, $I_2$, and $I_3$. For several angstroms of Cu on CdS, new ELS features (shaded) appear which are not due to the bulk Cu or CdS. These features change with increasing metal cov-

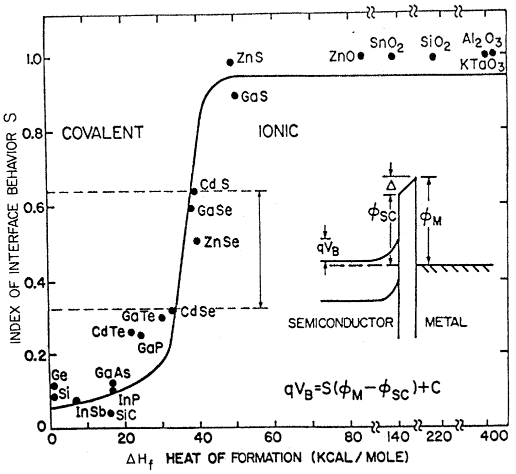

FIG. 1. Index of interface behavior (Ref. 5) $S$ plotted vs heat of compound formation. Dashed lines indicate $S$ range spanned by CdS and CdSe.

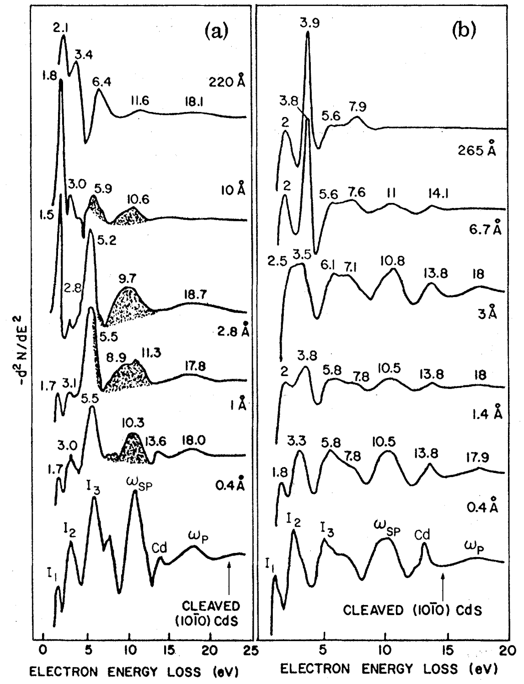

FIG. 2. Electron-loss spectra of reactive vs unreactive interfaces as a function of metal overlayer coverage: (a) Cu on cleaved CdS (10$\bar{1}$0); features unrelated to bulk Cu or CdS are shaded; (b) Ag on cleaved CdS (10$\bar{1}$0).

erage, eventually corresponding to losses of the bulk metal.[9] Analogous features appear for Cu and Ag on CdSe(11$\bar{2}$0). Furthermore, the adsorbed Cu Auger features are chemically shifted from those of bulk Cu. In contrast, no dramatic changes occur for Ag on the same CdS(10$\bar{1}$0) surface under identical conditions. With increasing Ag coverage, the spectra manifest only a slowly changing superposition of Ag and CdS features.

The indication of M-SC reactivity from ELS spectra can be used to estimate a critical heat of reaction $\Delta H_R{}^c$ for metals with CdS and CdSe. Chemical heats of reaction $\Delta H_R$ for most common metals with CdS and CdSe are listed in Table I. These $\Delta H_R$ were calculated per metal atom for the reaction $M + (1/x)CA \rightarrow (1/x)[M_xA + C]$ from $\Delta H_f$'s[10] of compound semiconductor $CA$ and most stable metal-anion product[11] $M_xA$, analogous to the $\Delta H_f$ calculations of transition metals on Si reported by Andrews and Phillips.[12] The stars in Table I indicate the most stable compounds at the interfaces probed with ELS. The extent of reactivity for Al, Ag, Cu, and Au on CdS and CdSe outlines a division between reactive versus unreactive interfaces at $\Delta H_R{}^c \sim 0.5$ eV per metal atom. Reactions occur for $\Delta H_R > 0$ due to the incomplete dissociation of semiconductor cations from the new interface molecules, which reduces the barriers to chemical reaction. The divisions in Table I demonstrate that most common metals react with CdS and CdSe. Furthermore, since covalent semiconductors are less stable against interface reaction than CdS or CdSe, these metals should react with these compounds as well. Clearly, for such M-SC junctions, the microscopic charge redistribution and atomic rearrangement associated with chemical reactions render any intrinsic surface states of the semiconductor irrelevant to the interfacial electronic properties.

TABLE I. Heats of reaction $\Delta H_R$ for common metals with CdS and CdSe. Stars designate interfaces studied with ELS. The division between reactive and unreactive interfaces indicates a critical heat of reaction.

| | METAL SULFIDE | $\Delta H_R$(eV/ metal atom) | METAL SELENIDE | $\Delta H_R$(eV/ metal atom) |
|---|---|---|---|---|
| Unreactive | ★ AuS | 3.94 | ★ AuSe | 1.36 |
| | $Bi_2S_3$ | 1.99 | HgSe | 1.05 |
| | HgS | 1.00 | $WSe_2$ | 1.05 |
| | | | $FeS_{0.96}$ | 0.75 |
| | | | $PtSe_{0.8}$ | 0.69 |
| | PtS | 0.69 | SnSe | 0.58 |
| | ★ $Ag_2S$ | 0.61 | ★ $Ag_2Se$ | 0.52 |
| | PbS | 0.53 | PbSe | 0.46 |
| | FeS | 0.51 | $Bi_2Se$ | 0.42 |
| Reactive | ★ $Cu_2S$ | 0.50 | ★ $Cu_2Se$ | 0.41 |
| | SnS | 0.43 | $In_2Se$ | 0.16 |
| | $WS_2$ | 0.41 | | |
| | $NiS_{0.67}$ | 0.29 | | |
| | InS | 0.16 | | |
| | CrS | 0.15 | | |
| | $TaS_2$ | -0.57 | MnSe | -0.10 |
| | ZnS | -0.58 | ZnSe | -0.15 |
| | GaS | -0.62 | $Ga_2Se$ | -0.20 |
| | MnS | -0.66 | ★ $Al_2Se_3$ | -0.69 |
| | $Cs_2S$ | -1.00 | | |
| | $Ti_2S$ | -1.27 | $TiSe_{1.5}$ | -1.00 |
| | ★ $Al_2S_3$ | -1.43 | MgSe | -1.54 |
| | MgS | -2.10 | $ThSe_{1.7}$ | -2.66 |
| | $ThS_{1.7}$ | -3.53 | | |

M-SC barrier heights also exhibit a systematic dependence on chemical reactivity. Figure 3 illustrates this relationship between $qV_B$ vs $\Delta H_R$ for a variety of metals on four compound semiconductors. Barrier heights were measured primarily by internal photoemission for semiconductors cleaved in vacuum.[6] Each curve yields a fit to the data points at least as good as linear plots of $qV_B$ vs $\varphi_M$ or $X$.[6]

In all four graphs, the fitted curves exhibit sharp changes in $qV_B$ at $\Delta H_R \sim \Delta H_R{}^c$ as determined for CdS and CdSe. The center of this tran-

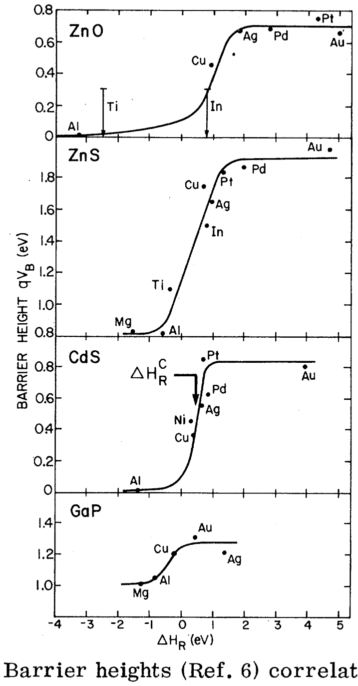

FIG. 3. Barrier heights (Ref. 6) correlated with heats of chemical reactivity for metals on ZnO, ZnS, CdS, and GaP.

sition occurs at 0.3 eV for CdS and ZnS. This transition center is higher for the more stable compound ZnO (0.4 eV) and lower for the less suitable compound GaP (−0.2 eV). Although these four semiconductors encompass a wide range of interface behavior, their $qV_B$ vs $\Delta H_R$ transition slopes vary by only a factor of 2 and exhibit no apparent dependence on chemical stability or ionicity. Similar plots for other metal–compound-semiconductor systems such as ZnSe and GaAs suggest analogous behavior. The linear dependence of $qV_B$ vs $\Delta H_R$ for transition metals on elemental Si corresponds to the left side of such a chemical reactivity plot, since $\Delta H_R < 0$ for all associated interfaces.[12] These correlations in terms of metal-semiconductor anion reactivity are also consistent with the $qV_B$ dependence on anion properties of Au-semiconductor junctions.[13] The extension of reactivity plots to other semiconductor systems appears to be limited only by the availability of electronic and thermodynamic information.

The agreement between the transition center of the reactivity plot and $\Delta H_R^c$ for metals on CdS suggests that low $qV_B$ on the left-hand side of the curves of Fig. 3 are related to reactive interfaces while high $qV_B$ on the right-hand side are due to unreactive junctions. Charge relocalization and atomic rearrangement can account for this barrier height transition qualitatively. The semiconductor barrier height depends on both microscopic dipole formation at the intimate M-SC contact and charge transfer to or from the semiconductor surface space charge region. Microscopic charge redistribution at the interface is commonplace and substantial, as evidenced by the many low-work-function metals on semiconductors which produce $n$-type Schottky barriers even though $\varphi_M - \varphi_{SC} < 0$.[6] This charge redistribution is driven by the difference in bulk exchange correlation energies[14] and has been observed[15] as electron tunneling from metal into semiconductor band gap.[16] The position with respect to the anions of metal atoms on or within the outermost semiconductor layer can also affect the direction and magnitude of charge exchange. One may hypothesize that the extent of compound formation controls both the local charge redistribution and atomic positions at the interface, thereby dominating the barrier heights.

In conclusion, ELS results and a striking correlation between M-SC barrier heights and chemical reactivities are reported here which strongly suggest replacing the concept of Fermi level pinning via intrinsic surface states by that of microscopic charge redistribution at the M-SC junction.

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