

ROLE OF CATION DISSOCIATION IN SCHOTTKY BARRIER FORMATION AT II–VI COMPOUND SEMICONDUCTOR–METAL INTERFACES*

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We used UV and X-ray photoemission spectroscopies to probe the relation between the chemical and electronic structure at ultrahigh-vacuum-cleaved CdS–metal and CdSe–metal interfaces. When combined with current–voltage and capacitance–voltage studies of the same interfaces in ultrahigh vacuum, the experimental results indicate that partially dissociated cadmium cations, produced as a consequence of interfacial chemical reaction, may be the electrically active species giving rise to the observed Fermi level stabilization at these contacts. The extent of cation dissociation, a spectroscopically determined quantity, is shown to correlate inversely with the measured Schottky barrier height. An indirect and modified doping effect is suggested as one possible mechanism to explain this behavior. Features of interdiffusion, in particular regarding the interfacial distribution of dissociated cadmium, are also described.

1. INTRODUCTION

Recent ultrahigh vacuum studies of metal–semiconductor interfaces have established the importance of metal-induced chemical reaction and interdiffusion in determining the nature of the electronic contact^{1–8}. In particular, a distinct transition in Schottky barrier height ϕ_{SB} with metal reactivity has been observed for a variety of compound semiconductors, described by the heat of reaction ΔH_{R} for the most stable metal–semiconductor anion product³. For III–V semiconductors, it has been shown that associated with this transition in ϕ_{SB} is a reversal in the stoichiometry of semiconductor out-diffusion, evidenced by changes in the measured surface cation-to-anion concentration ratio⁹. This suggests two chemically distinct regimes of barrier formation which can lead to the formation of electrically active sites of different types (*e.g.* defects^{7,8,10}), which in turn can yield different Fermi level pinning positions within the semiconductor band gap⁹. For II–VI semiconductors, however, qualitatively different interdiffusion behavior has been observed, and in particular no well-defined reversal in out-diffusion stoichiometry

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has been found¹¹. In addition, metals on II–VI semiconductors produce many intermediate barrier heights between the reactive and unreactive limits^{3,4,11–13}, in contrast with the discrete pair of levels reported for metals on the (110) faces of GaAs⁷, GaP¹² and InP⁸. These differences suggest that at II–VI contacts mechanisms other than simple defect pinning levels may be playing a role in ϕ_{SB} formation as well.

In this paper we present experimental evidence which links a partially dissociated cadmium phase at contacts to CdS or CdSe with the Schottky barrier formation. Cadmium is dissociated from the semiconductor lattice as a consequence of metal–anion compound formation, the extent of dissociation being determined by the strength of metal–anion chemical bonding and/or possible metal–cadmium alloy formation. The cadmium dissociation energy scales with the Fermi level position and in this sense can be used to parameterize ϕ_{SB} . We also demonstrate a practical means of controlling the interfacial distribution of dissociated cadmium using Al/Au and Au/Al interlayer contacts.

2. INTERFACE PREPARATION AND CHARACTERIZATION

The CdS and CdSe samples were as-grown ultrahigh purity single crystals (n type with a resistivity of about 1 Ω cm and with $(E_c - E_F)_{Bulk} \approx 0.1$ eV) supplied by Cleveland Crystals, Inc. After applying ohmic indium back contacts in a dry nitrogen atmosphere, we mounted the specimens on a carousel manipulator for *in situ* cleavage and subsequent metal deposition. All interfaces were prepared and characterized in the same stainless steel ultrahigh vacuum chamber (with a base pressure of about 6×10^{-11} Torr) with facilities for UV and X-ray photoemission spectroscopies (UPS and XPS) as well as current–voltage (J – V) and capacitance–voltage (C – V) analysis. At each successive stage of metal deposition, photoemission measurements monitored spectral features characteristic of surface atomic bonding and interdiffusion. For the J – V and C – V measurements, an array of 0.5 mm dots was evaporated through a metal mask in close proximity to each cleaved semiconductor face. Using this approach, photoemission spectral features could be unambiguously correlated with actual current transport properties. Additional experimental details can be found in refs. 11 and 13.

3. RESULTS AND DISCUSSION

Not only new surface chemical reaction but also the position of the surface Fermi level in the band gap can be monitored by following the evolution of the UPS Cd 4d and valence band levels as functions of the metal overlayer thickness. Here we make use of the intense and highly monochromatic He I (21.2 eV) and He II (40.8 eV) discharge lines for UPS. It is instructive to consider aluminum, gold and Al/Au contacts since limiting barrier behavior is observed for these metals, and furthermore we have shown that, by increasing the thickness of an ultrathin aluminum interlayer (less than 2 Å) at Au/CdS and Au/CdSe contacts, the effective ϕ_{SB} can be continuously reduced to zero¹³.

The He II UPS spectra of Figs. 1 and 2 illustrate features of band bending and reaction for Al/Au and Au/Al contacts to CdS(11 $\bar{2}$ 0) respectively. The position of the Cd 4d level for the cleaved surface (Fig. 1) corresponds to the flat-band starting

condition¹¹. The slight downward shift for two-monolayer (1 monolayer (ML) = 3.6×10^{14} atoms cm^{-2}) aluminum coverage (-0.2 eV to greater binding energy) indicates movement of the Fermi level toward and possibly above the conduction band edge, consistent with the observed tendency of aluminum to form ohmic contacts on CdS and CdSe^{11,12}. Upon subsequent deposition of 10 \AA of gold, a reverse 0.7 eV shift is observed indicating movement of the Fermi level away from the conduction band edge (n-type band bending). The same ultimate 0.7 eV shift is observed for gold contacts without the aluminum interlayer¹¹. Qualitatively similar behavior has been reported for an aluminum interlayer at the Cu–CdS(11 $\bar{2}$ 0) interface¹⁴. Thus the gold-induced pinning position remains unchanged by the aluminum interlayer for aluminum thicknesses of less than 2 ML, *i.e.* the mechanism by which the aluminum interlayer reduces the effective ϕ_{SB} ¹³ apparently does not involve a change in the surface Fermi level pinning position. It appears, therefore, that the aluminum interlayer contacts for II–VI semiconductors provide examples of interfaces where $E_c - E_F$ photoemission measurements of ϕ_{SB} are not strongly related to effective J – V and C – V barrier heights, a point which will be discussed further elsewhere¹⁵.

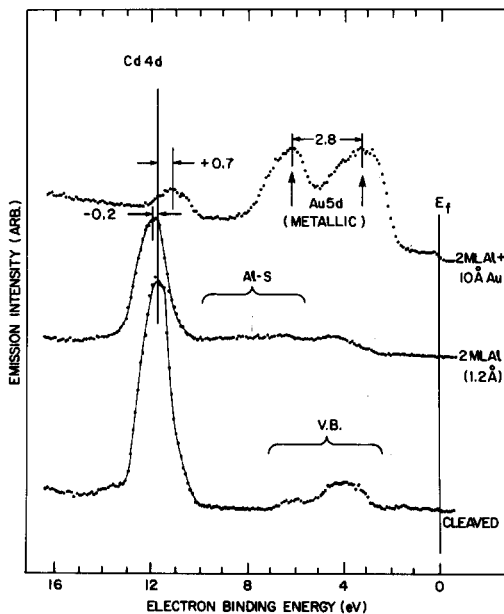


Fig. 1. He II ($h\nu = 40.8$ eV) UPS spectra of the valence band and Cd 4d level for CdS(11 $\bar{2}$ 0) as a function of successive aluminum and gold depositions (temperature, 300 K).

Changes in the valence band structure are also indicated in Fig. 1. The various features in the cleaved surface spectrum between 3 and 7 eV can be understood to a first approximation in terms of bulk electron states^{11,16}. The filling in of emission in the region from about 6 to 10 eV for 2 ML of aluminum is attributed to an Al–S reaction^{11,17}. Characteristic Au 5d features are observed for 10 \AA of gold, where the 2.8 eV spin–orbit splitting indicates a bulk metallic-like phase^{18,19}. The fact that this phase is not obtained until much higher coverages (more than 40 \AA) for gold-only

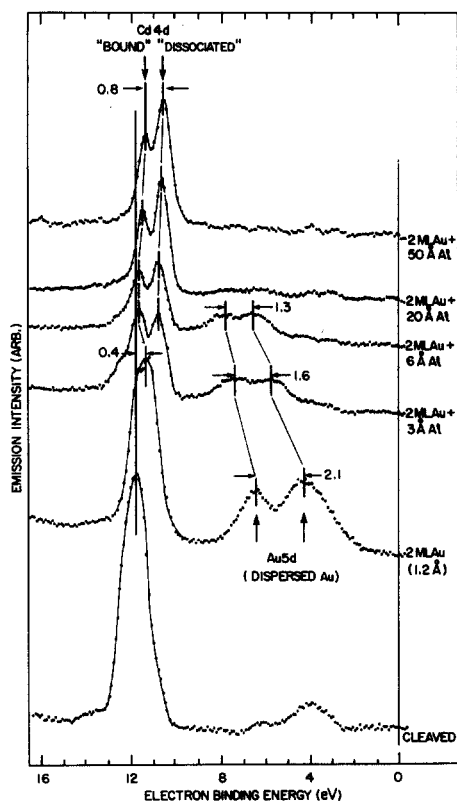


Fig. 2. He II ($h\nu = 40.8$ eV) UPS spectra for successive gold and aluminum depositions onto CdS(11 $\bar{2}$ 0) (temperature, 300 K).

contacts¹¹ indicates that the reacted Al-S layer effectively blocks Au-CdS interdiffusion, leading to a more abrupt interface.

Dramatically different behavior is observed if we maintain the interlayer thickness but reverse the order of deposition of the metals (Fig. 2). The initially deposited gold induces a 0.4 eV Cd 4d shift, incomplete for 2 ML coverage, and associated with this the decreased Au 5d spin-orbit splitting of 2.1 eV indicates a dispersed gold phase^{18,19}. With subsequent aluminum deposition the shifting to greater binding energy and further narrowing of the Au 5d manifold is strongly similar to valence band trends observed for a series of progressively gold-deficient Au-Al alloys, *i.e.* Au₂Al, AuAl and AuAl₂¹⁸, but is less like trends seen for gold diluted into cadmium films¹⁹. Also apparent is the pronounced 0.8 eV splitting of the Cd 4d level into "bound" and "dissociated" peaks (Fig. 2) which has been attributed to cadmium in normally coordinated and partially dissociated lattice states respectively^{11,17}. The separation energy between these states, a quantity we denote as Δ (dissociated cadmium), is taken as a measure of the extent of cadmium dissociation: the greater Δ (dissociated cadmium), *i.e.* the greater the relative displacement of the "dissociated" cadmium peak to smaller binding energies, the greater is the extent of dissociation.

The 0.8 eV splitting value for Δ (dissociated cadmium) is characteristic of

aluminum, whereas smaller splittings are observed for less reactive metals such as copper or gold¹¹. This trend is illustrated in Fig. 3, where care has been taken to select metal coverages such that "bound" versus "dissociated" peak heights are roughly equal in each case. In this way we avoid the usual difficulties associated with locating closely spaced overlapping peaks. Thus differences in the splittings, even though comparable with the nominal 0.2 eV experimental resolution, are easily resolved. In addition we note that the measured splittings are quite reproducible.

In Fig. 4(a) we show that Δ (dissociated cadmium) for different metals can be empirically correlated with the heat of metal-anion reaction ΔH_R . Thus it may be that the formation of new metal-chalcogen interface compounds involves incomplete dissociation of the displaced cadmium cations. Since it has already been shown that ΔH_R can be correlated with ϕ_{SB} ^{3,4}, it follows that in turn Δ (dissociated cadmium) can also be used to parameterize ϕ_{SB} . This is shown in Fig. 4(b). Figures 4(a) and 4(b) both provide correlations between a macroscopic property (*i.e.* ΔH_R or ϕ_{SB}) and Δ (dissociated cadmium), an interface-specific spectroscopically measured quantity.

A physical basis for this parameterization can be postulated based on the known ability of excess free cadmium to act as an n-type dopant^{20,21}, thus enhancing injection through the metal-semiconductor interface. In fact low

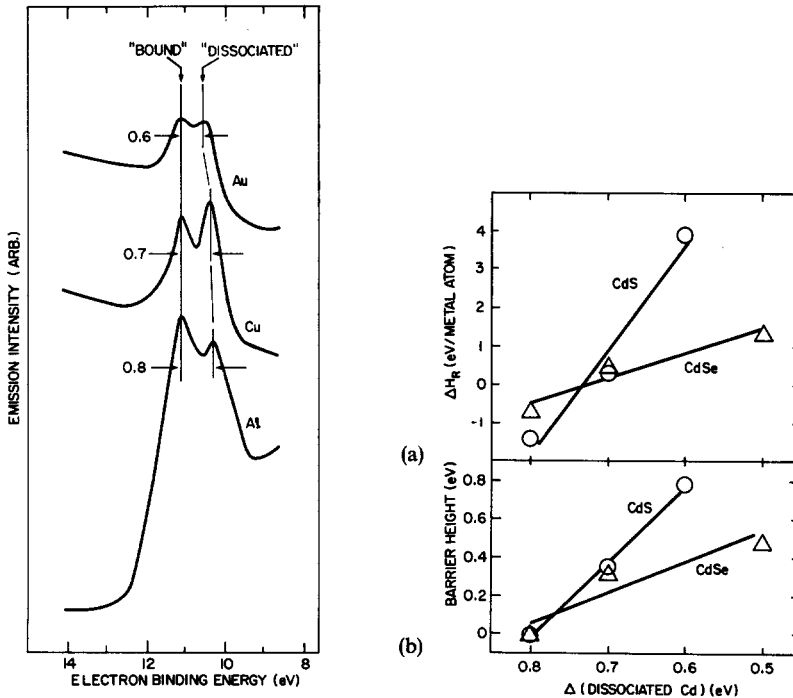


Fig. 3. Selected He II spectra of the Cd 4d region for gold (20 Å), copper (40 Å) and aluminum (5 Å) contacts to CdS(1010) showing the energy separation of "bound" and "dissociated" cadmium phases (see text). The spectra are aligned with respect to the "bound" Cd 4d peak for gold.

Fig. 4. Correlation of Δ (dissociated cadmium) with (a) the metal-anion heat of chemical reaction for metals on CdS (O) and CdSe (Δ) (after ref. 3) and (b) the measured Schottky barrier heights^{11,12}.

resistivity CdS and CdSe are customarily prepared simply by allowing a cadmium excess to develop in the as-grown material²². Based in part on these observations, Freeman and Slowik²³ have recently proposed that cadmium released as a consequence of chemical reaction at contacts to CdS or CdSe leads to an indirect doping effect, thereby reducing ϕ_{SB} proportionately. Thus the degree of dissociation of cadmium, whether loosely bound to reacted metal-chalcogen species or involved in metal-cadmium alloying interactions, could have significant bearing on its doping ability, *e.g.* the position of the dopant donor level, the probability of donor ionization and the in-diffusion and spatial distribution of donors into the subsurface space charge region. With regard to possible metal-cadmium alloy formation, we note that gold and cadmium are miscible over their entire concentration range^{19, 24}, copper and cadmium also show appreciable alloying tendencies²⁴ while aluminum and cadmium are virtually immiscible at all concentrations²⁴. Thus, metal-cadmium alloying behavior could be used to explain the trend in Δ (dissociated cadmium). Furthermore, we cannot rule out the possible effect of classical metal alloy work function variation on ϕ_{SB} ²⁵. Most likely, however, the mechanism of Fermi level stabilization at these contacts involves a combination of effects, including spatially extended doping near the interface, the details of which we are currently investigating.

One further observation concerns the remarkably large amount of surface cadmium, both bound and free, which persists even for 50 Å of aluminum coverage (Fig. 2). In fact the cadmium signal is observed to *increase* slightly between 6 and 50 Å of aluminum, although we hesitate to speculate on the significance of this because of uncertainties in sample realignment following evaporation, possible changes in surface morphology and other effects which might alter the absolute signal intensity. Nevertheless, there is an unmistakable enhancement of cadmium out-diffusion and/or metal in-diffusion in comparison with the aluminum interlayer

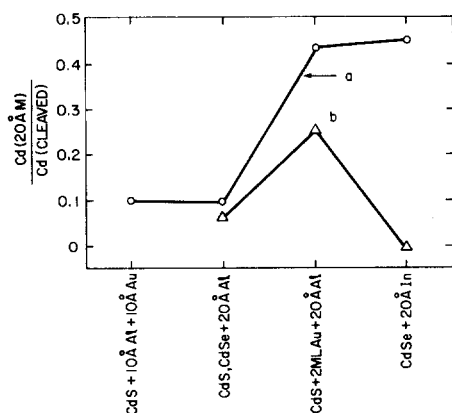


Fig. 5. Relative surface cadmium concentrations for ohmic contacts to CdS and CdSe: curve a, Cd 3p_{3/2} XPS ($\hbar\omega = 1487$ eV) core level peak areas for single and interlayer metal contacts normalized to the cleaved surface values (total cadmium); curve b, proportion of dissociated cadmium determined from the ratio of "dissociated" to "bound" peak areas in the He II UPS spectra (*e.g.* Fig. 3). The data are arranged horizontally in order of increasing total cadmium signal. The contact thickness in each case is roughly 20 Å.

case (Fig. 1). This may be due to an enhanced dissociation of the semiconductor sublattice by gold in-diffusion, analogous to effects reported for near-noble metals on silicon²⁶. In Fig. 5 we compare the relative surface cadmium concentrations measured for these and other contacts via XPS core level analysis^{11,13,27}. Also indicated, where it could be determined from the UPS spectra, is the proportion of dissociated cadmium. It can be seen that the distribution of dissociated cadmium can be varied with some degree of control. For example, aluminum contacts with and without a gold interlayer form excellent ohmic contacts^{11,27}. Without the interlayer the dissociated cadmium is apparently displaced into the subsurface lattice whereas with the interlayer it is drawn into the metal contact region. The combination Al(10 Å)/Au(10 Å) leads to a relatively abrupt junction, with no surface cadmium detectable via UPS¹³, although the more bulk-sensitive XPS analysis indicates a substantial cadmium concentration in the near-surface region. By way of contrast, indium, which itself is an n-type dopant²⁸, forms an ohmic contact with no release of dissociated cadmium¹¹. This ability to tailor the nature and distribution of interdiffused dopant atoms at the interface could have applications in practical device fabrication, especially where forming or aging treatments have been observed to enhance interdiffusion and thereby to alter diffused contact properties (see, for example, ref. 29).

4. CONCLUSIONS

In summary, we have suggested that a partially dissociated cadmium phase may give rise to electrically active interface species which stabilize the Fermi level at metal contacts to CdS and CdSe. The cadmium dissociation energy, a spectroscopically measured and interface-specific quantity, is shown to scale with the measured Schottky barrier height, a reflection of the different degree of chemical bonding that takes place between metal, anion and cation. The continuous variation in Schottky barrier height for different metal contacts to II–VI semiconductors can be accounted for by this picture, which may involve an indirect and modified doping mechanism. Features of metal and cadmium interdiffusion and reaction are elucidated, with implications for control of diffused contact properties in practical device applications.

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