

METAL CONTACTS TO II–VI SEMICONDUCTORS: CdS AND CdTe

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Schottky barrier heights have been measured for a series of metals on atomically clean and oxidized CdS and CdTe crystals. Interface reactions have also been studied by X-ray photoemission. Conventional linear models are quite unsatisfactory to account for the barrier heights for different metals. Differences in stoichiometry at the interface are shown to influence barrier heights emphasizing the importance of defects in these systems.

1. Introduction

The application of modern “surface science” experimental techniques, in conjunction with conventional methods such as current–voltage and capacitance–voltage, has led to substantial improvements in our understanding of the physics of metal–semiconductor interfaces. The most detailed and thorough investigations have been carried out for metals deposited on atomically clean semiconductor surfaces and it is now well known that such interfaces are, very often, not atomically abrupt. By and large, the nature of reactions and reaction products at such boundaries are quite well understood and have been investigated extensively for Si, Ge and III–V semiconductor–metal combinations [1]. However, the fundamental mechanisms governing the formation of electrical barriers at interfaces are not well understood. It is clear that several mechanisms may contribute to Schottky barrier formation; these include bonding at the interface, disorder, defect, and metal induced gap states (MIGS). The relative importance of the various mechanisms contributing to the electrical barriers depend on the metal–semiconductor combination and on preparation conditions, in ways that are not fully understood.

The II–VI semiconductors CdS and CdTe are important materials in past attempts to obtain a systematic pattern of Schottky barrier heights at metal–semiconductor interfaces. Early investi-

gators assumed that the linear model, where the barrier heights (ϕ_b) vary linearly with metal work function (ϕ_m) or electronegativity, could be applied in a straightforward manner [2]. Based on such analysis it was reported that CdTe and CdS straddle the so-called covalent–ionic transition, that is, a large dependence of ϕ_b on ϕ_m was reported for CdS but not for CdTe [2]. More recently the existence of this transition has been called into question [3].

In this paper we report a detailed investigation of metal interfaces to clean and air exposed CdS single crystals and consider the data together with those obtained for the metal–CdTe system [4,5]. We show that the linear model is, in general, quite inapplicable. Furthermore, chemical reactions occur readily between CdS and a number of metals leading to ageing effects associated with Schottky barrier diodes. In general it is believed that the electrical barrier formation at these interfaces is substantially influenced by interface defect formation.

2. Experimental

The crystals of n-CdS used in these investigations were obtained from Eagle Picher Inc. and had a carrier concentration of $\sim 10^{16} \text{ cm}^{-3}$. Ohmic back-contacts were made using a In:Ga eutectic. Diodes were fabricated by depositing 0.5 mm di-

ameter circular metal contacts on atomically clean CdS crystals prepared by cleavage in ultra-high vacuum, or alternatively on crystals cleaved in the atmosphere. Schottky barrier heights were established using I - V and C - V techniques. Chemical interactions at the metal-CdS interfaces were probed using X-ray photoelectron spectroscopy in a VG Scientific high resolution ESCALAB instrument. Metals were deposited in amounts varying from sub-monolayer to several tens of Å and following each evaporation the XPS spectra were recorded.

3. Results

Diodes formed for metals on clean CdS in general showed a behaviour consistent with thermionic emission across an interface barrier, and for barriers greater than 0.4 eV the ideality factors were close to unity. Barriers smaller than 0.3 eV could not be accurately established by I - V and

C - V techniques. Many diodes showed a time dependence where the effective barrier height increased with time; these increases are demonstrated by arrows in fig. 1.

Fig. 1 shows a plot of the measured barrier heights against the metal work function, not only for vacuum cleaved but also for air cleaved surfaces. It is immediately clear that the barrier heights span a large range of energies, up to 1 eV. For some metals, e.g. Pd, there appears to be a dependence of ϕ_b on the nature of the CdS surface, whereas for others the barriers measured for clean and air exposed surfaces are practically identical.

Shifts of the Fermi level were also probed as a function of increasing overlayer thickness, using the XPS techniques. For the clean surface the bands are reasonably flat with the separation of the valence band edge and the Fermi level at the surface being within around 0.2 eV of the CdS band gap. By and large these results indicate the development of barrier heights in reasonable agreement with those shown in fig. 1. In particular

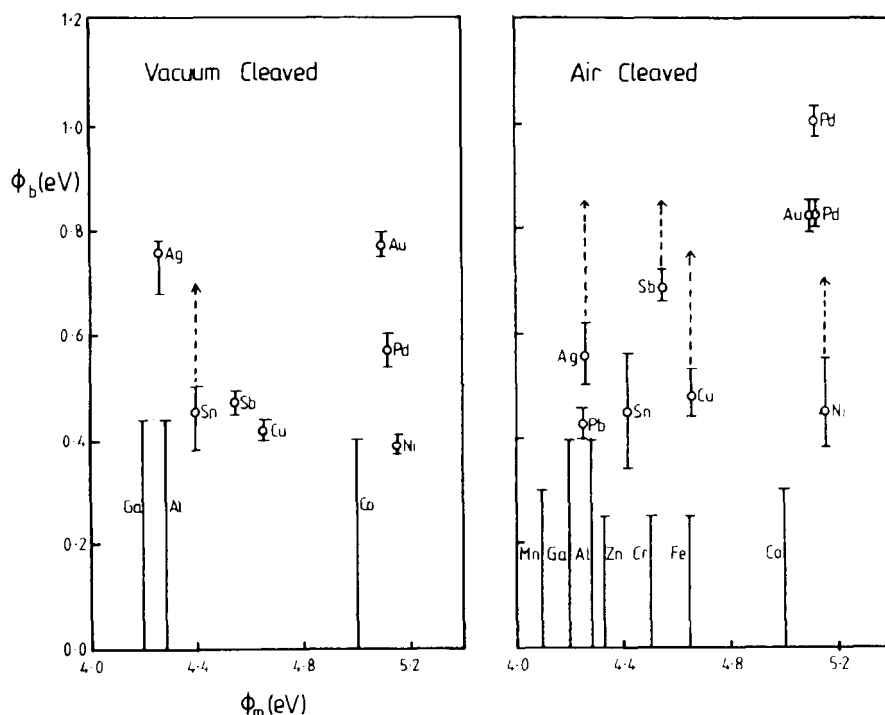


Fig. 1. Plots of Schottky barrier height versus metal work function for metals on vacuum and air cleaved CdS.

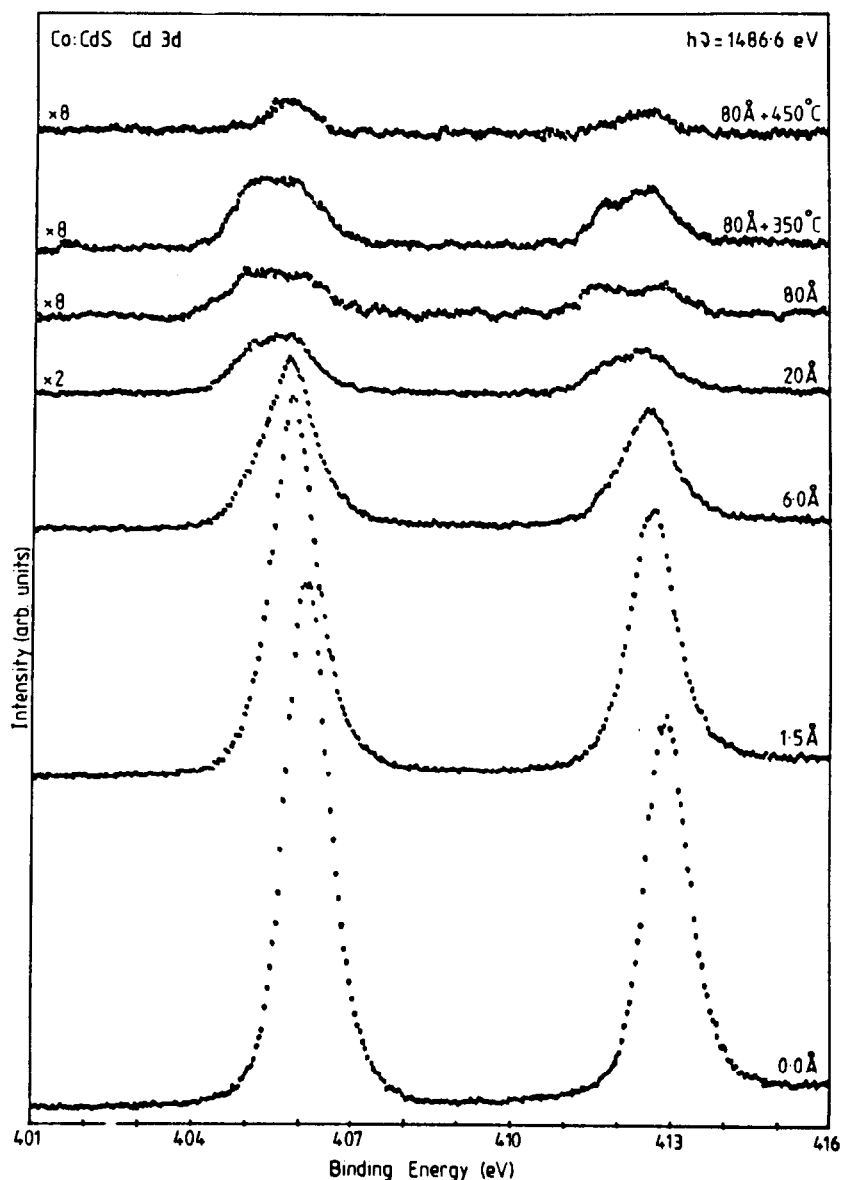


Fig. 2. XPS data of the Cd 3d emission for increasing coverages of Co on vacuum cleaved CdS.

aluminium appeared to lead to exceedingly low barriers with E_F at the interface being located in the vicinity of the conduction band edge. The interpretation of these data should be treated with caution in view of the time dependence of barrier heights, and in view of the difficulties of extracting accurate barrier height values from photoemission. However, within the limitations they do lend

full support to the data for the barrier heights shown in fig. 1.

XPS investigations demonstrate that some metals lead to strong chemical reactions with the CdS surface. An example of this is given in fig. 2, here for the case of Co. As the overlayer thickness increases the Cd 3d photoemission features split into two components, as the CdS surface is disso-

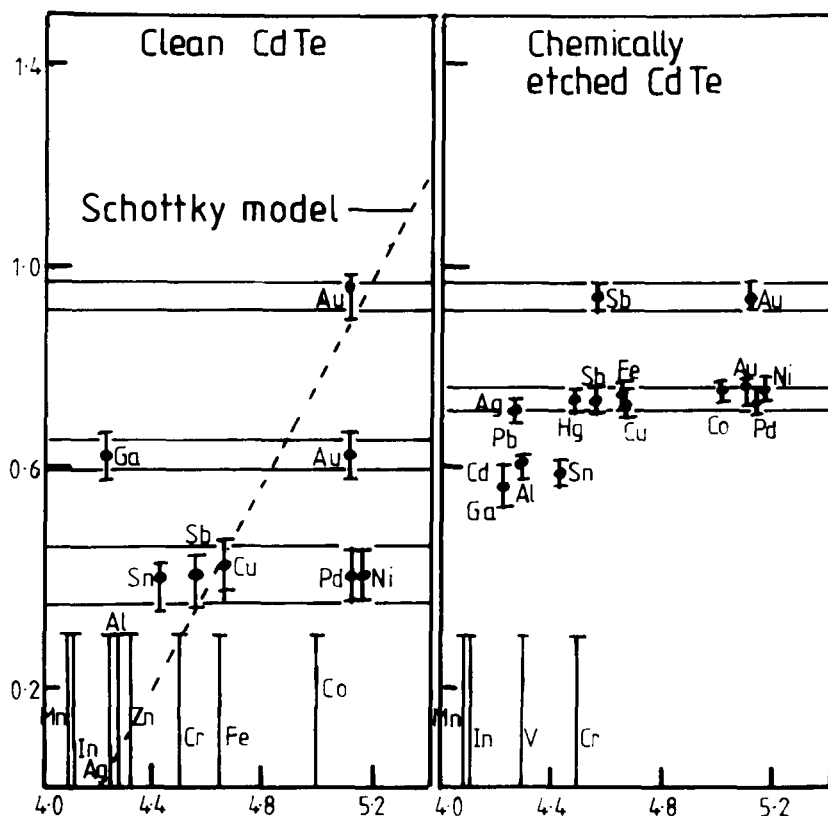


Fig. 3. Plots of Schottky barrier height versus metal work function for metals on vacuum cleaved and chemically etched (1%Br-methanol) CdTe.

ciated. This is confirmed by a similar broadening of the S2p emission. Of the metals studied, Co, Al and Pd reacted strongly with the CdS surface, whereas Ag and Sb reacted only weakly or not at all.

Similar data of barrier heights for metals on clean and oxidised CdTe surfaces are presented in fig. 3. Again it may be seen that the barriers cover a large energy range. It is of interest to note the barrier heights for gold on clean CdTe as well as for Sb and Au on chemically etched crystals. Here, two values of barrier heights are obtained, even for contacts prepared under apparently identical conditions. The cause of these differences is associated with the precise stoichiometry of the interface and is discussed further in the subsequent section.

4. Discussion

For metals on CdS and CdTe the values of barrier heights extracted using different techniques are in reasonable agreement. This fact, as well as comparison with more limited data obtained by others [6], gives us considerable confidence in the values presented in figs. 1 and 3. Although, by and large, the barrier heights tend to increase with increasing work function, it is quite clear that a linear model is not appropriate for the data presented in figs. 1 and 3. Linearity is not improved by using electronegativities of the metals, rather than work function. It was pointed out in the introduction that CdS and CdTe are key materials in the so-called covalent-ionic transition, which was based on the assumption of a

linear relationship between ϕ_b and ϕ_m (or X_m). Since this linear relationship is clearly not observed it is incorrect to include CdS and CdTe in the plot, and indeed the very existence of the transition must be in doubt [3]. Previous studies by us and others for metals on clean GaAs [7] and InP [8] also calls into question the applicability of the linear model and the existence of any covalent–ionic transition.

Brillson [6] has attempted to classify the reported barrier heights for metals on CdS surfaces in terms of the thermodynamic parameters associated with the constituents at the interface. Metals which reacted readily with sulphur were classified as yielding low barriers whereas unreactive metals, on the other hand, were suggested to form large barriers. In the present more extensive investigation it is clear that this analysis is too simple, since metals such as Pd are reactive with sulphur but yield large barrier heights. Nevertheless, the thermodynamic analysis introduced by Brillson has been found to describe reactions at the interfaces particularly well, provided interaction of the adsorbed metal with anions and cations in the substrate is fully considered.

Fermi level pinning by metal induced gap states, or MIGS, has been extensively discussed in the literature [9,10]. The band gap at the surface may close on account of the presence of the metal pinning E_F close to the charge neutrality level ϕ_0 . For CdTe Tersoff's calculations [10] suggest that ϕ_0 should lie about 0.7 eV below E_c but to our knowledge no such calculation has been conducted for CdS. It is clear that MIGS alone cannot account for the data reported in figs. 1 and 3. Pinning of E_F by interface states is dependent on the density of those states and it is possible that this is lower at CdS–metal interfaces than at CdTe or GaAs–metal boundaries [11]. However, if MIGS dominated, one might expect some smooth dependences of ϕ_b on ϕ_m or X_m and this is not observed.

An unusual feature of the data for the CdTe–metal barrier heights is observed for Au in fig. 3. Here it is seen that Au yields barriers of ~ 0.6 and 0.92 eV, even though the contacts for the two situations were prepared in the same way, Kuech [12] previously reported unusual behaviour for Au

contacts on clean CdTe. He found that Au yielded $\phi_b \approx 0.6$ eV, Cd gave values ~ 0.4 eV, but an Au/Cd alloy contact yielded a value of ϕ_b of ~ 0.92 eV. These differences were ascribed to pinning by defects which were related to stoichiometry changes at the interface. These effects have been investigated further in these studies, concentrating on the chemically etched

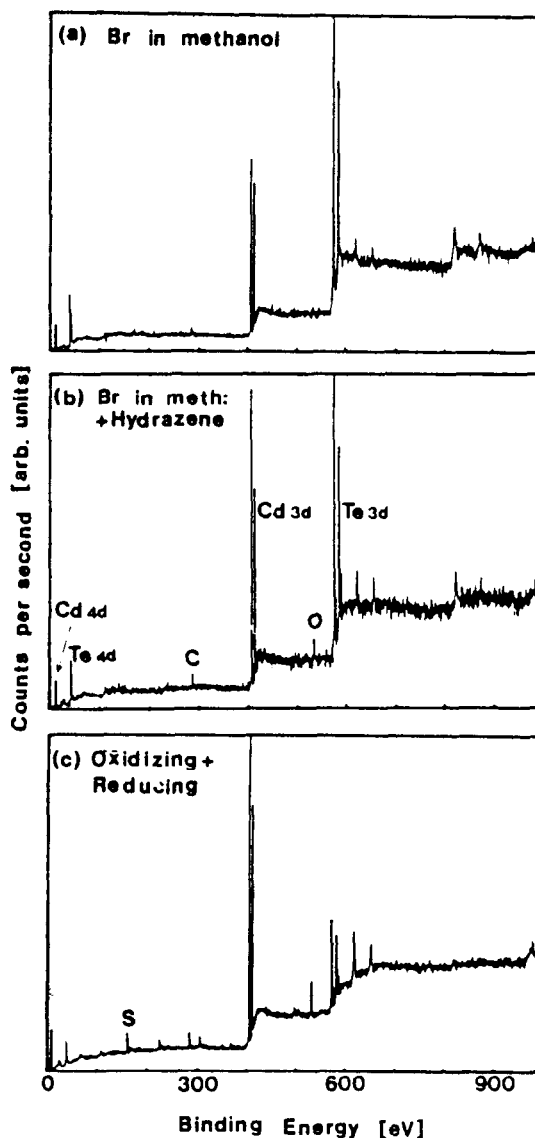


Fig. 4. XPS data for etched surfaces of CdTe: (a) etched in 1%Br–methanol, (b) Br–methanol+hydrazene and (c) an oxidising + a reducing agent.

surfaces where the surface stoichiometry can be varied by chemical means.

Fig. 4 shows XPS data for CdTe surfaces prepared using different chemical etchants. One of these left the surface Te rich or Cd deficient (top), and another left the surface Cd rich or Te deficient (bottom). Gold or antimony contacts on the Cd-rich surface led to barrier heights of 0.92 eV whereas the Te-rich surface yielded barriers of 0.72 eV. Furthermore, photoluminescence investigations [13] have demonstrated that deep levels are generated by the respective etching procedures at energies corresponding to those where Fermi level pinning is observed. These studies strongly indicate that the different Schottky barrier heights are associated with deep levels resulting from Cd or Te related deficiencies. Furthermore, several metals such as Co lead to extreme dissociation of the CdTe interface causing further complications due to alloying and disorder.

There are strong reasons for believing therefore that the measured barrier heights for metals on CdTe are significantly influenced by defects and changes in interface stoichiometry. In view of the fact that similar reactions are observed at metal–CdS interfaces it is reasonable to suppose that similar effects would be applicable. Our over-

whelming impression, therefore, is that defects associated with reactions at the interface have very substantial effects on Schottky barriers to CdS and CdTe.

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