

LETTER TO THE EDITOR

Schottky barriers to CdS and their importance in Schottky barrier theories

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Abstract. A study of the transport properties of Schottky barriers to the vacuum- and air-cleaved surfaces of CdS have yielded a wide range of barrier heights which, contrary to popular belief, show no linear correlation with the metal work function. The characteristics have shown a strong dependence on the methods of preparation and subsequent treatment of the diodes. Further investigations using xps have confirmed that the interfacial chemistry is significant in the Schottky barrier formation process. These results are considered in terms of various Schottky barrier theories and the importance of localised interface states is emphasised.

In order to gain a better understanding of the physics associated with electrical barrier formation at metal–semiconductor interfaces it is traditional to measure barrier heights for a wide range of metal–semiconductor combinations and to search for a pattern which can be explained by simple models of the interfaces. It has been assumed in the past [1] that the Schottky barrier heights at intimate interfaces are linearly dependent on the work function and electronegativity of the metal contact. Based on an analysis of data in terms of a linear model it has then been concluded that interface states give rise to strong Fermi level pinning in covalent semiconductors, but to little or no pinning for the more ionic semiconductors such as CdS. This so-called covalent–ionic transition has received considerable attention in the literature and it is still widely believed that the linear model on which it is based is applicable for metal–semiconductor interfaces in general. We have previously shown that the linear model [1] is inapplicable for the more covalent materials such as InP and CdTe [2, 3]. In this communication we also show that it is inapplicable for CdS, a material which has been reported as being on the ionic side of the covalent–ionic transition.

Simple models show that Schottky barrier heights may vary linearly with metal electronegativity if there is a constant density of interface states in the band gap of the semiconductor. The existence of localised states, however, such as those produced by chemical reactions at the interface can lead to gross deviation from constant state density. For the III–V semiconductors InP and GaAs it is known that chemical reactions can severely influence the interface and this has also been seen for the limited range of metals which have

previously been studied on CdS [4]. In view of the importance of CdS in Schottky barrier theory we have therefore undertaken a full and detailed investigation of a range of metals on clean and air-cleaved CdS surfaces. We show that contrary to popular belief the linear model is not applicable and that chemical reactions are indeed common.

In these investigations n-CdS crystals with a carrier concentration of about 10^{16} cm^{-3} obtained from Eagle Picher Inc. were used. Metal contacts of 0.5 mm diameter were deposited by vacuum evaporation on to atomically clean CdS surfaces prepared by cleavage in ultra-high vacuum. Similar contacts were also deposited on to crystals cleaved in the atmosphere in order to evaluate the influence of surface oxides on contact properties. Schottky barrier heights were measured by I – V and C – V techniques, under normal atmospheric conditions. Changes in contact properties were monitored as a function of time, and in some instances following annealing of the contact in an inert atmosphere. Chemical interactions at the metal–CdS interfaces were monitored by x-ray photoelectron spectroscopy (xps) in a VG Scientific ESCALAB. Metals were deposited in amounts varying from sub-monolayer to thick coverages on to cleaved CdS surfaces and following each evaporation the xps spectra were recorded. The influence of annealing on these contacts was also investigated.

Figure 1 shows a plot of the measured Schottky barrier heights for ten metals on vacuum cleaved CdS and 15 metals on air-cleaved crystals. In general the I – V behaviour of diodes displaying barriers greater than 0.4 eV was well described by thermionic emission theory and values of barrier height were extracted by

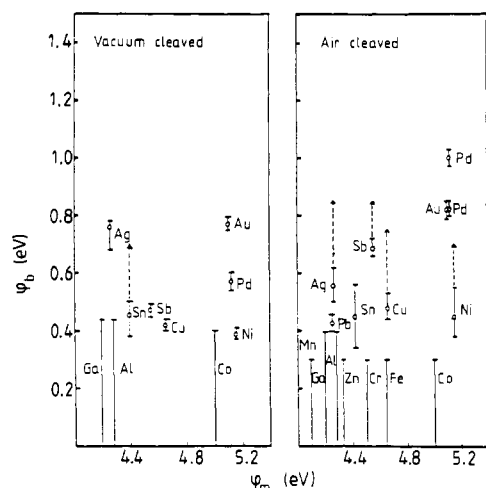


Figure 1. Barrier heights from I - V versus metal work function for metals on vacuum- and air-cleaved CdS. The upward arrows show the extent of the increase in barrier heights resulting from aging or annealing.

suitable curve fitting [5]. Barrier heights measured by the C - V method are in quite good agreement. Barriers smaller than around 0.3 eV could not be readily measured by I - V and C - V techniques and are therefore referred to as ohmic contacts. Several points are immediately clear from figure 1. Some of the metals yield ohmic contacts, but others including the more electronegative Au and Pd yield large barriers. However, for some metals there is a substantial dependence of the barrier height on time and where this resulted in an increase in the barrier height it is represented by an upward arrow in figure 1. There also appears to be a difference in barrier height for a few metals, for example Pd, on vacuum-cleaved and air-cleaved CdS surfaces. In addition a small dependence on the quality of the cleavage is observed in some cases. The 'aging' effects indicate changes in the nature of the

interface, perhaps due to chemical reactions or to interdiffusion, and for the case of Ag on air cleaved CdS similar changes could be generated by heat treatment, i.e. by accelerated aging effects. Similar effects for metals on CdTe are known to be associated with chemical reactions at the interface and for this reason the xps studies are highly relevant for the metal-CdS systems.

In this programme we have carried out an extensive study using high-resolution xps for Au, Ag, Pd, Sb, Sn, Al and Co on clean cleaved and oxidised CdS surfaces. Typical xps spectra are shown in figure 2 for increasing coverages of Pd on vacuum-cleaved CdS. The Cd_{3d} and S_{2p} core level emissions are shown and several interesting features can be seen. Both the Cd and S emission move to lower binding energy in the first 6 Å of Pd coverage due to band bending. Evidence of the formation of palladium sulphide is seen in the S_{2p} emission where an extra component appears at higher binding energy which is caused by S bonding in a Pd environment. In addition to this a chemically shifted component appeared towards lower binding energy in the Cd_{3d} core lines which is due to 'free' Cd released from the interface on formation of palladium sulphide. The Pd_{3d} emission also appeared chemically shifted at low coverages because of its bonding to S. On annealing further reactions are seen to occur.

Among the other metals whose interfaces with CdS were studied Al and Co were seen to react in a similar manner to Pd, forming metal sulphides and releasing Cd from the interfaces. Sn was also seen to bond with the surface, however no 'free' Cd was seen and it is believed that Sn bonded to S at the interface without disrupting the CdS surface. Following this initial layer subsequent Sn deposition led to islands on the surface, i.e. Stranski-Krastanov growth [6]. Sb and Ag on CdS did not appear to react with clean CdS, i.e. the core levels are not chemically shifted though Sb is believed

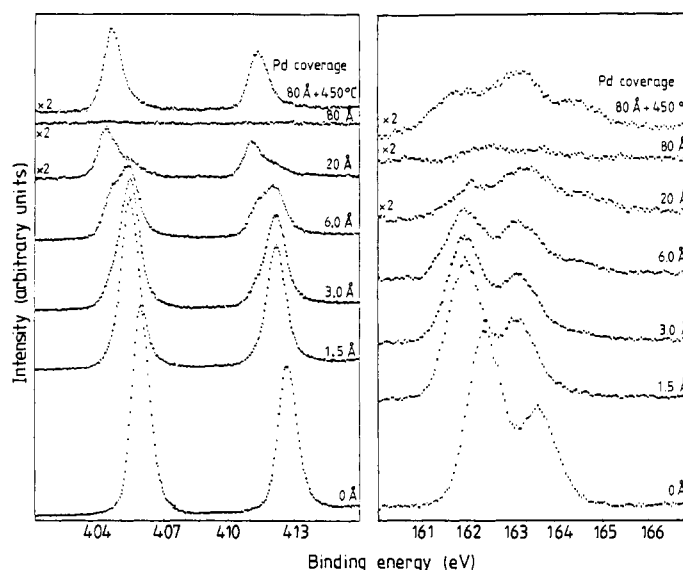


Figure 2. xps spectra of the Cd_{3d} and S_{2p} core levels for increasing Pd coverages on vacuum-cleaved CdS.

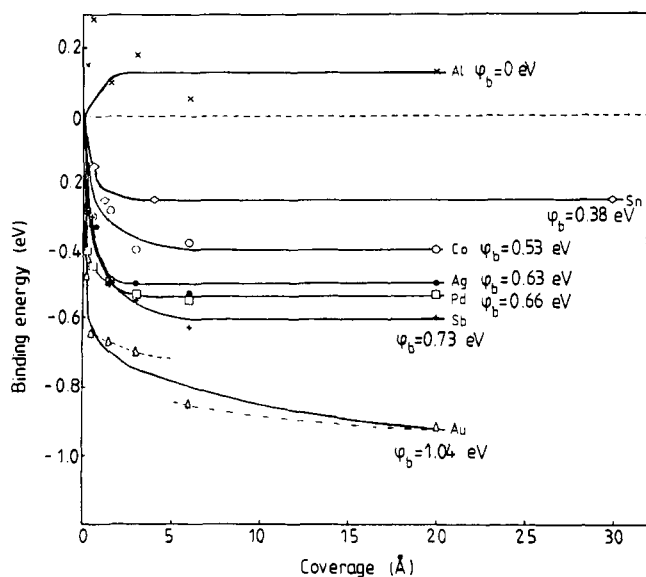


Figure 3. Plots of the Cd_{3d} core level shift versus coverage for metals on vacuum cleaved CdS from xps. The S_{2p} core level shift normally agreed well with those shown here.

to react with the oxide on the air-cleaved surface. Au appeared to disrupt the CdS surface causing some out-diffusion of S. These interactions will be discussed in more detail in future publications [7].

The formation of Schottky barriers for ultra-thin coverages of metal has also been explored by xps. The shifts of the Cd_{3d} and S_{2p} core level emission can be used to monitor the movement of the Fermi level near the CdS surfaces. For CdS it is relatively easy to distinguish such Fermi level shifts from 'chemical shifts' associated with interface reactions. Calculations from the $C-V$ data suggest that the Fermi level is located at about 0.13 eV below the conduction band for bulk CdS. If no initial shifts occurred at the cleaved CdS surface, then the Fermi level shifts as seen in the xps data would represent the band bending. A study of the valence band spectra from xps confirms that the Fermi level position at the CdS surface is very close to the conduction band edge, i.e. the bands appear to be flat before metal is deposited. The barrier heights shown in figure 3 have therefore been obtained by adding 0.13 eV to the xps core level shifts, except for the case of aluminium where it was subtracted rather than added. Here again the barrier heights measured are in reasonable agreement with those measured by $I-V$ showing a similarly wide range of behaviour, but some of the values are not exactly the same, for example, gold which is somewhat large and silver which is low. However, it must be emphasised that large errors are associated with the determination of barrier height from photoemission measurements.

It is clear from the data presented that different metals do indeed give rise to a wide range of electrical barrier heights when deposited on clean or air-cleaved CdS crystals. However, it is also abundantly clear that the data of figure 1 cannot be described by a straight line, i.e. the linear model does not describe this system,

contrary to popular belief. The use of electronegativities rather than work functions does not improve matters. The situation is very similar to that observed for metals on CdTe [3]. Chemical reactions clearly occur at the interface with some metals interacting strongly with the anion, some with the cation, and some with both. Broadly speaking it is possible to understand the origin of these reactions in terms of thermodynamic data published for CdS, for bulk metal sulphides and for Cd-metal alloys. This will be considered in more detail elsewhere [7].

The two main mechanisms that appear important in the theory of electrical barriers at metal-semiconductor interfaces are metal-induced gap states, or MIGS [8], and pinning of the Fermi level by defects [9]. MIGS are expected to pin E_F close to the middle of an effective gap, and according to Tersoff [10] the pinning energy, i.e. the charge neutrality level will not differ greatly for different metals [10]. It certainly may be that such a mechanism does operate for the less reactive metals. Chemical reactions, however, will inevitably lead to defects and disorder at the interface, and if present in sufficient numbers the defect associated pinning will dominate the interface behaviour. We believe that this is the reason for the wide range of electrical barrier heights observed for metals on CdS. It is clear then that the data presented here are inconsistent with a linear model. These data, as well as those for CdTe and the III-V semiconductors calls into question the whole basis of the analysis leading to the so-called 'covalent-ionic' transition in Schottky barrier formation.

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