Schottky barrier modulation at metal contacts to CdS and CdSe

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Soft x-ray photoemission spectroscopy measurements have been used to study the pinning position of the surface Fermi level as well as the nature of the electrostatic band bending for single and interlayer metal contacts to ultrahigh-vacuum-cleaved CdSe and CdS $(10\bar{1}0)$ surfaces. Single metal (Al,Au) contacts are found to exhibit a one-to-one correspondence between the pinning position and the effective Schottky barrier height as measured by *in situ* C–V and I-V analyses. However, a fundamentally different mechanism of barrier modulation is indicated for interlayer contacts, i.e., contacts formed by interspersing an ultrathin reactive metal interlayer (Al) between the semiconductor and a noble metal contact (Au). Core level broadenings as a function of photon energy are interpreted in terms of sharp band bending at the surface, leading to the possibility of quantum mechanical tunneling through the barrier. This barrier narrowing effect is attributed to an indirect doping effect as a consequence of metal–semiconductor interfacial reaction.

I. INTRODUCTION

The effective Schottky barrier height at ultrahigh vacuum (UHV) cleaved surfaces of the II–VI compound semiconductors, CdS and CdSe, can be modulated over a wide range (0.8 and 0.5 eV, respectively) in two distinct ways. The first, and most obvious, simply entails the use of different contact metals. For metals spanning a wide range of work function and reactivity (Al,In,Cu, and Au), we have observed a one-to-one correspondence between the pinning position of the surface Fermi level and the effective Schottky barrier height, based on combined photoemission and *in situ* capacitance–voltage (C–V) and current–voltage (I–V) measurements.[1] Similar observations for other semiconductors[2–4] have produced confidence in the photoemission technique as a reliable indicator of barrier heights.

The second way, certainly less obvious, entails the use of two metals in combination, e.g., a reactive-less reactive metal pair, where reactivity is defined in terms of the heat of reaction for metal–semiconductor anion compound formation.[5] For example, by varying the thickness of an ultrathin Al (reactive) interlayer between the semiconductor and a Au (less reactive) contact, the effective Schottky barrier height can be *continuously* modulated over the full range for metals on CdS, CdSe.[6] (Al and Au were in fact chosen because they produce limiting behavior in terms of barrier heights for CdS, CdSe, i.e., Al yields ohmic contacts and Au yields close to maximum barriers.[1,7]) Yet for interlayer contacts, the Au-induced Fermi level pinning position remains unaltered by the Al interlayer (Ref. 8, confirmed in this work). This is significant because it provides an example of an interface where photoemission measurementss of barrier heights are apparently not strongly related to effective C–V and I–V barrier heights. Of particular interest, therefore, is the mechanism by which the barrier is modulated. Previous electrical measurements have indicated a substantial nar-rowing of the surface space-charge layer with increasing interlayer thickness, suggesting the possibility of quantum mechanical tunneling to explain the barrier reduction.[6]

In this paper, we employ soft x-ray photoemission spectroscopy (SXPS) to further investigate the barrier formation process for interlayer contacts, in particular the detailed nature of the electrostatic band bending. Monochromatized synchrotron radiation was employed in order to vary the escape depth of the photoelectrons by changing the exciting photon energy. We observe a broadening of the Se $3d$ energy distribution curve (EDC) as the photon energy is decreased from the surface ($\hbar\omega = 130$ eV) to the bulk ($\hbar\omega = 70$ eV) sensitive regime, corresponding to the sampling of a wider range of binding energies. After careful elimination of other possible broadening effects, we attribute this to a marked narrowing of the energy band bending region, thus lending additional support to the possibility of electron tunneling through the barrier. An indirect doping effect as a consequence of metal–semiconductor reaction is suggested to explain this behavior.

II. EXPERIMENTAL

The SXPS experiments were conducted at the University of Wisconsin Synchrotron Radiation Center using the Brown–Lien "Grasshopper" monochromator[9] and a double pass cylindrical mirror analyzer (CMA). The interlayer interfaces were formed by sequential evaporation of Al and Au onto room-temperature, UHV-cleaved CdSe $(10\bar{1}0)$ surfaces. The samples were as-grown ultrahigh purity single crystals [n-type, $\sim 1\Omega$ cm, $(E_C - E_F)_{\text{bulk}} \sim 0.1$ eV] supplied by Cleveland Crystals, Inc. Nominal metal film thickness was monitored by a quartz crystal oscillator positioned next to the cleaved surface. During evaporation, the chamber pressure typically rose from a base of 4×10^{-11} Torr to the low

10^{-10} Torr range. Angle integrated SXPS spectra were obtained at each successive stage of metal deposition. Overall energy resolution was better than 0.3 eV.

III. RESULTS AND DISCUSSION

Figure 1 shows Se $3d$ core level EDC's as a function of photon energy recorded during formation of a CdSe/Al/Au interlayer contact. Core level shifts due to changes in band bending[1,8] have been removed in these spectra to enable a detailed comparison of peak widths and asymmetries. For each photon energy the spectra are normalized to the incident photon flux. The variation of electron escape depth with electron kinetic energy is also included in Fig. 1 to roughly deliniate what is meant by "surface" versus "bulk" sensitive: For Se $3d$ photoelectrons (binding energy ~ 60 eV), maximum surface sensitivity (less than 10 Å) is achieved for photon energies around 130 eV. The inclination of the CMA axis with respect to the surface normal (roughly 45°) enhances the surface sensitivity even further. For decreasing photon energies the escape depth increases rapidly but is highly material dependent.[10] For CdS and CdSe it is probably somewhat less than the 90–100 Å implied in Fig. 1(c).[11]
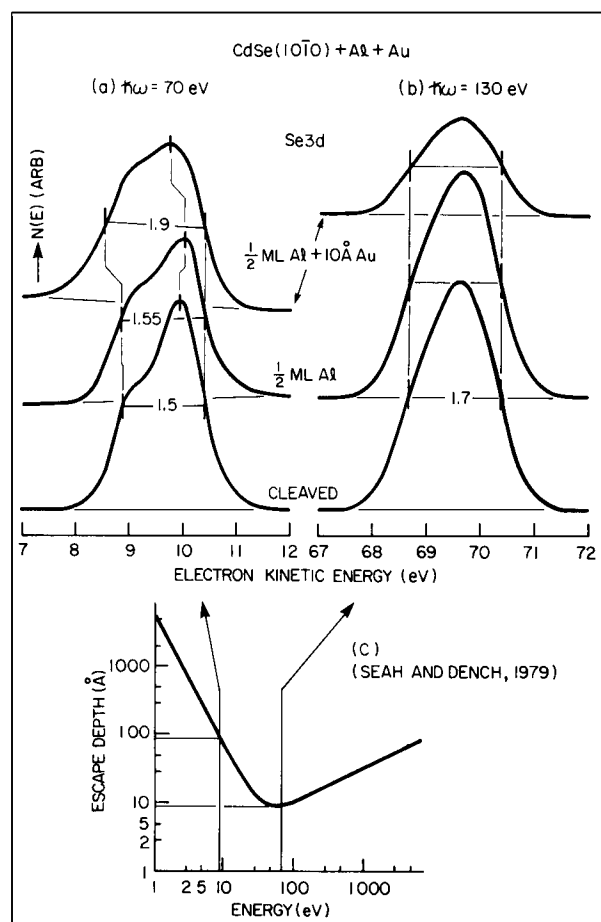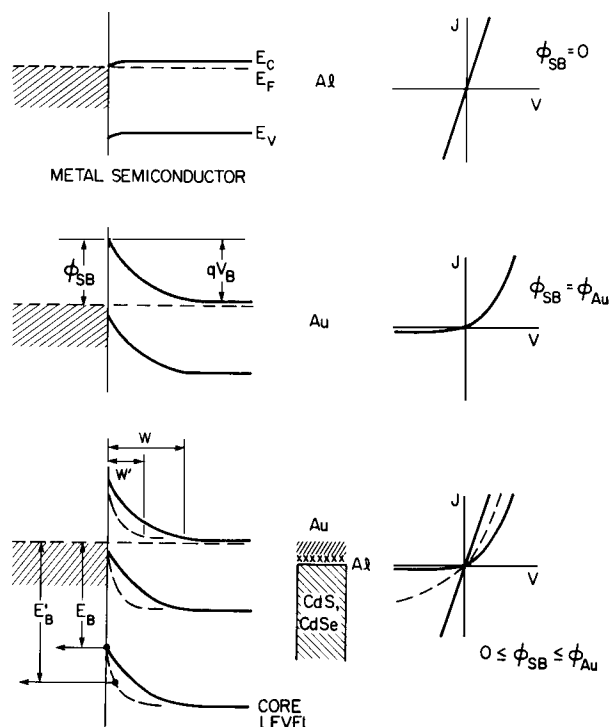

FIG. 2. Correlation of energy band bending profiles inferred from photoemission measurements (left) with current–voltage characteristics (right) for single metal (top, middle) and interlayer (bottom) contacts to UHV-cleaved CdSe, CdS($10\bar{1}0$) surfaces. qV_B denotes the band bending ϕ_{SB} the associated Schottky barrier height, W the barrier width over which all or most of the band bending takes place, and E_B the electron binding energy.

In discussing these results it will be helpful to consider, at the same time, the schematic energy band profiles for contacts to CdS, CdSe shown in Fig. 2. Also shown here are schematic I-V characteristics corresponding to these profiles. The top two panels illustrate the previously mentioned correspondence between photoemission-derived pinning positions and electrically derived barrier heights for Al and Au contacts. The bottom panel illustrates the continuous modulation of I-V characteristics between the single metal limits for the interlayer contact. Here the pinning position is the same as for the Au contact.

In order to test the possibility of a barrier narrowing effect for the interlayer case, let us postulate the existence of sharp band bending at the surface (dashed profiles, bottom Fig. 2). In the case where the photoelectron escape depth is small in comparison to the width W of the electrostatic band bending region, the EDC's so obtained yield the binding energy E_B of the core level with respect to the Fermi energy at the surface. If, on the other hand, strong electrostatic band bending occurs near the surface, and the photoelectron escape depth can be increased sufficiently, the $E_C - E_F$ separation may change appreciably over the escape depth region. Since core levels should follow the electrostatic potential which produces the band bending, under these conditions the binding energy of the photoelectrons will depend on the electron escape depth which in turn will depend on the exciting photon energy (W', E'_B, Fig. 2).

In agreement with these ideas, the EDC's of the fully developed interlayer contact (Fig. 1, top) show a broadening

FIG. 1. Se $3d$ photoemission spectra for (a) $\hbar\omega = 70$ eV, and (b) $\hbar\omega = 130$ eV at successive stages of interlayer contact formation on CdSe($10\bar{1}0$). The spectra are recorded as a function of the as-collected kinetic energy for the cleaved surface case. Alignment is with respect to right-hand full width at half maximum points. One monolayer (ML) equals 3.5×10^{14} atoms/cm^2. An electron escape depth curve is shown in (c), after a recent compilation for inorganic compounds by Seah and Dench.[10]

(1.7 to 1.9 eV) with increasing escape depth, corresponding to the sampling of a wider range of binding energies. Initially, for the cleaved surface, the width of the bulk sensitive EDC (1.5 eV) is less than that for the surface sensitive EDC (1.7 eV) due to improved monochromater resolution at the lower photon energy. With this improved resolution the Se $3d$ spin orbit splitting is partially resolved. The width of the surface EDC remains constant at 1.7 eV throughout the contact formation. The strong attenuation of the surface Se $3d$ signal after 10 Å Au deposition is consistent with the relatively abrupt nature of interlayer junctions.[8,12] The fact that an ultimate width of 1.9 eV is obtained in the bulk EDC is verification that the lack of broadening in the surface EDC cannot be ascribed simply to limited instrumental resolution. There may also be a slight broadening to 1.55 eV in the bulk EDC upon Al interlayer deposition, consistent with the small band bending effects associated with Al contacts (1,8, Fig. 2). One can also observe that changes in the symmetry of the bulk EDC can be shown to follow from the sense of the band bending, i.e., downward for Al and upward for Au (Fig. 2). Downward band bending would lead to enhanced emission at lower binding energies for large escape depths, consistent with the shift of the peak maximum for the Al EDC to higher kinetic energies. Conversely, upward band bending induced by subsequent Au deposition would lead to a shift of the peak maximum to lower kinetic energies, as observed.

It is important, in the interpretation of the data in Fig. 1, to eliminate other possible sources of broadening, such as surface core level shifts, charge transfer due to chemical bonding, and differential final state relaxation energies. Surface core level shifts have been reported for Si,[13] GaAs and GaSb,[14] and $5d$ metals,[15] but are less likely for more ionic II–VI semiconductors since the lattice termination represents less of a perturbation on the surface atom valence electronic structure. A shift in the Se $3d$ binding energy for surface atoms, if present, must at any rate contribute less than 0.2 eV broadening, i.e., the difference between bulk and surface peak widths for the cleaved surface. Furthermore, some of this 0.2 eV difference has already been attributed to broadening introduced by the monochromator, thus restricting the possible contributions of surface core level shifts to even smaller values. Chemical bonding shifts are ruled out by the observation that no comparable broadening of the bulk EDC occurs for single metal contacts, i.e., Al or Au alone, in spite of the known tendency for metal–chalcogenide (e.g., Al_2Se_3) compound formation at these interfaces.[1] Likewise, there is no reason to expect any broadening contribution from differential relaxation screening energies for the interlayer case, if not present for single metal contacts.

On the basis of these observations, we therefore conclude that associated with the reduction in effective barrier height at interlayer contacts is a pronounced decrease in the width W (Fig. 2) over which most of the band bending takes place. One possible mechanism to explain this barrier narrowing is a strong n-type doping effect induced at the surface by the interlayer metal. The space–charge layer would then become very thin and conduction would take place by quantum mechanical tunneling. An indirect mechanism whereby metal–chalcogen chemical reaction leads to an excess of dissociated

Cd in the surface space–charge region, which in turn produces an n-type doping effect,[16] has in fact been proposed[17] and refined[8] for metal contacts to CdS and CdSe. We note that low resistivity n-type CdS and CdSe crystals are customarily prepared simply by allowing a Cd excess (or equivalently, a chalcogen deficiency) to develop in the as-grown material.[18] In support of the metal-induced doping hypothesis, C–V analysis of interlayer contacts imply, in addition to a decrease in the width of the space–charge layer, an increase in the effective donor density as the interlayer thickness is increased.[6] Group III Al atoms might also act as impurity donors, although we consider this less likely due to the strong chemical reaction observed for Al at the semiconductor surface, especially for monolayer Al coverages.[1,8] By way of contrast, In (also group III) shows no evidence for chemical reaction[12] and does produce a direct doping effect.[19]

This barrier narrowing effect may thus be directly analogous to thin highly doped surface tunneling layers produced by ion implantation at Si Schottky diodes,[20] a significant difference being that for CdS and CdSe the doping effect may be induced by the contacting (interlayer) metal itself. We note that the donor density and thickness of such a highly doped layer required for desired barrier height lowering of Schottky contacts has been theoretically modeled.[21] We have empirically prescribed the *interlayer* thickness required for a given barrier lowering at CdS, CdSe,[6] but the density and distribution of dissociated Cd, thought to be the electrically active species, is more difficult to ascertain.[8] Considerations of the type in Ref. 21, however, imply that the ratio of effective donors released into the surface space–charge region per interlayer atom is much less than one, a conclusion also reached in Ref. 1 from a somewhat different point of view.

Finally, while we cannot deduce quantitatively the probability for electron tunneling from our data, we can place an upper limit on the *total* width of the CdSe/Al/Au band bending region. This follows from the observation that the broadening in the bulk EDC (1.5 to 1.9 eV, Fig. 1) is equal to the magnitude of the Au-induced band bending, i.e., 0.4 eV. Thus the entire band bending must occur within the electron escape depth region, i.e., ~ 100 Å or less.

IV. CONCLUSIONS

Data is presented which suggests a barrier-narrowing mechanism of Schottky barrier modulation at interlayer metal contacts to CdS and CdSe. By suitable choice of metal or metal combinations, a means of independently controlling not only the Fermi-level pinning position but also the width of the energy band bending region is demonstrated. An indirect self-doping process due to metal-induced chemical reaction is discussed as a possible new contribution to the Schottky barrier formation process.

ACKNOWLEDGMENTS

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