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Polar Ligand Adsorption Controls Semiconductor Surface Potentials

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Abstract: Controlled surface modification of CdTe single crystals and CdTe and CuInSe$_2$ solar cell quality thin films was achieved by chemisorption of a series of organic ligands with varying dipole moments. Contact potential difference measurements in air showed that adsorption of benzoic or hydroxamic acid derivatives on the thin films or crystals changes the semiconductors' electron affinity without significantly affecting band bending. The magnitude and direction of surface potential changes, which reach 670 mV between extreme modifications, correlate with the ligands' dipole moments. Ligand dipole moments were controlled by varying the substituents of the ligand. Quantitative Fourier transform infrared (FTIR) spectroscopy showed that benzoic acid surface coverage is about one monolayer. Finally, FTIR spectral analysis showed that the benzoic acid derivatives adsorb via coordination to Cd on CdTe and that hydroxamic acids bind to Cd on CdTe and to In on CuInSe$_2$. These phenomena occur in several systems (two semiconductor compounds, two types of binding groups, and two types of surface morphologies were examined) and may prove useful in band edge engineering.

Introduction

Control over the surface chemistry and physics of semiconductors is essential for constructing semiconductor devices and fine tuning their electrical performance. This is particularly true for polycrystalline semiconductor devices, such as CdTe- and CuInSe$_2$-based solar cells. Here we show that semiconductor work functions (surface potentials) can be controlled by chemisorbed polar organic ligands even in air, which is where most applications take place.

Among inorganic chemical treatments used for surface passivation, we note hydrogen,[1-3] halogens,[4] Ru^{3+},[5-7] Cs,[8] O$_2$,[9,10] and S^{2-}.[11-15] Organic ligands offer greater flexibility for surface modification than inorganic treatments because of the possibility of incorporating two or more functional groups, which can be modified systematically and independently, into a single molecule. Thus, an organic molecule can be designed to possess (i) functional groups for surface binding and (ii) auxiliary functional groups for the introduction of additional properties such as polarity, hydrophobicity, or light sensitivity.[16]

Previous studies showed that exposure of semiconductors to organic ligands can change semiconductor luminescence[17-24] or flat band potentials.[25-28] In those studies the semiconductor properties were shown to vary with ligand concentration. For the case of aniline derivatives, the semiconductor photoluminescence intensity was found to depend on the substituents' Hammett parameters.[19] Most recently, experiments with gaseous boranes showed a correlation between ligand Lewis acidity and semiconductor photoluminescence intensity.[17]

We thought that organic molecules that would possess functional groups for surface binding as well as auxiliary groups that would change the molecules' dipole moments could provide a powerful means for modifying semiconductor surfaces in a predetermined fashion. We thus selected benzoic and benzohydroxamic acid derivatives for several reasons. Firstly, hydroxamic acids were expected to bind effectively to the semiconductor surfaces because they are good metal chelating agents. Benzoic acids were expected to adsorb on semiconductor surfaces because other carboxylic acids were known to adsorb on ZnSe.[29] Secondly, one can monitor surface binding by FTIR (Fourier transform infrared) spectroscopy, due to the presence of the strongly absorbing carbonyl group. Thirdly, the use of phenyl

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derivatives could allow systematic modifications of the dipole moments of the molecules by changing the para-substituents.

Here we provide direct evidence by FTIR spectroscopy that benzoic and benzohydroxamic acids adsorb onto CdTe and $CuInSe_2$ surfaces. Surface binding is shown to involve coordination to Cd on CdTe and In on $CuInSe_2$. We demonstrate further, by contact potential difference (CPO) measurements, that surface binding changes the surface potential of semiconductors. Moreover, surface binding is shown to affect mainly the semiconductor's electron affinity without significantly affecting band bending. Between extreme modifications, the surface potential changes span ranges of up to 670 mV for CdTe thin films, 570 mV for single crystal CdTe, and 600 mV for $CuInSe_2$ thin films. Most significantly, the extent of surface potential changes is shown to correlate with the ligands' dipole moments for both families of binders that were examined.

Experimental Section

Materials. Semiconductors. Single crystals of (111) oriented n-CdTe (100 Ω cm) were purchased from II-VI Inc., Saxonburg, PA, and intrinsic (111) oriented single crystal of CdTe were obtained from Soreq Nuclear Research Center, Israel. For attenuated total reflectance (ATR) FTIR spectroscopy, we used parallelepiped shaped CdTe plates (50 × 10 × 3 mm, 45°, purchased from Harrick Scientific). We note that the ATR substrate, made of hot pressed powder, will expose many different crystal faces as was checked experimentally, using electron channeling patterns in the scanning electron microscope. Polycrystalline p-type $CuInSe_2$ (CISe) films, deposited on Mo-coated glass substrates, were obtained from the Institut für Physikalische Elektronik Stuttgart.[30] Electroplated polycrystalline n-type CdTe films on SnO_2:F/soda lime glass substrates were prepared at the University of Queensland, Brisbane.[31] CdTe powder (Cerac, <5 mesh), used for adsorption isotherms, was examined by scanning electron microscopy and found to have an average particle diameter of about 10 μm. X-ray powder diffraction showed only peaks characteristic of CdTe.

Chemicals. Benzoic acid derivatives and *N*-benzoyl-*N*-phenylhydroxylamine (diphenylhydroxamic acid, DPH) were commercially available and were used as received. *N*-methylbenzohydroxamic acid derivatives were prepared by a procedure modified relative to that reported in the literature.[32] *N*-methylbenzohydroxamic acid was prepared as follows: 20 g (0.239 mol) of *N*-methylhydroxylamine hydrochloride was suspended in 150 mL of dry chloroform (dried by filtration through basic alumina) and treated with 80 mL (0.57 mol) of triethylamine. After 30 min, 34 mL (0.29 mol) of benzoyl chloride was added dropwise, and stirring continued for 2.5 h at room temperature. Then, the mixture was diluted with chloroform (300 mL), washed three times with 1 N aqueous $NaHCO_3$, three times with water, three times with 1 N aqueous HCl, and again with water, dried with $MgSO_4$, and concentrated in vacuo. Crude material (42 g) was obtained. The product showed one major spot on TLC which gave a color reaction with ferric chloride (silica gel, $CHCl_3$:MeOH (95:5) as the eluent), indicating the presence of a hydroxamate group. IR ($CHCl_3$): ν 1621 cm^{-1}. NMR ($CDCl_3$): δ 3.4 (s, 3H), 7.5 (m, 5H). Chromatography of the crude material on silica gel using gradients of chloroform and methanol provided the chromatographically pure product as an oil. Absorption of the ferric complex: (aqueous methanol, NaOAc buffer) λ_{max} = 426 nm (ϵ = 1870). Similarly, we prepared the *p*-methoxybenzohydroxamic acid derivative (mp 103–108 °C; lit.[32] 109–112 °C), *p*-nitrobenzohydroxamic acid derivative (mp 169–173 °C; lit.[32] 176–178 °C), and *p*-(methylsulfonyl)benzohydroxamic derivative (mp 148–150 °C).

Cadmium benzoate was precipitated from a solution of sodium benzoate upon additon of $CdCl_2$. The precipitate was redissolved in H_2O, and the insoluble portion was removed by filtration. The H_2O was evaporated and the compound dried at 120 °C. Cd and In complexes of DPH were synthesized by a literature procedure.[33] For analysis, hydroxamate and benzoate salts were dissolved in 0.15 M HCl in 50% (v/v) aqueous methanol. Ligand content was then determined by UV spectroscopy and metal content by atomic absorption. All ligand–metal ratios were within 5% of the expected values. Cadmium complexes of *N*-methylbenzohydroxamic acid complexes were synthesized by the same procedure as DPH, but metal–ligand ratios were about 1:1 (within 15%) instead of 2:1. An alternate procedure[34] also gave a 1:1 ratio.

Solvents used for syntheses were distilled, while those used for ligand adsorption were HPLC or spectroscopic grade. Rinsing solvents were analytical grade or better.

Procedure. Substrate Pretreatment. Prior to each adsorption experiment on single crystals, the CdTe crystals were immersed in boiling methanol (MeOH) for several minutes, polished with 0.05-μm alumina paste, rinsed ultrasonically in deionized water, etched for 2 min in 1% (v/v) Br_2/MeOH, rinsed in MeOH, etched for 15 min in 80 or 100% hydrazine hydrate (Merck), and rinsed in MeOH and deionized water (>10 MΩ cm resistivity). ATR substrates were immersed in boiling MeOH followed by acetonitrile or chloroform prior to adsorption. Thin films were immersed in boiling MeOH and acetonitrile before use. The CdTe films were subsequently etched for 10 min in 80% hyrazine hydrate and rinsed in deionized water. In the case of the CdTe thin film used in the FTIR measurements, the hydrazine etch was only 3 min. The CISe films were etched in an aqueous solution of 5% (w/w) KCN and 2% KOH (w/w) and rinsed in deionized water. CdTe powder was used without pretreatment.

Ligand Adsorption. To adsorb molecules on semiconductor crystals and films, we immersed the substrate in a 5 mM solution of the ligand in acetonitrile for 10 min and subsequently dabbed the substrate dry to remove excess solvent and solute. The adsorption procedure on thin films used for grazing angle FTIR was different. The film was exposed for 10 min to a 5 mM solution of DPH in acetonitrile, and subsequently, excess ligand was precipitated on the sample by allowing a few drops of the solution to evaporate. Finally the sample was rinsed with a 5 or 1 mM solution of DPH in acetonitrile. The acetonitrile used for the thin film FTIR experiments was taken from a newly opened bottle or filtered through basic alumina to minimize the water content.

CPD Measurements. We measured the CPD in air using a Kelvin probe apparatus (Besocke Delta-Phi, Jülich, Germany). This method is explained in ref 35. Here we will summarize its principle. A compensating electrical circuit is used to measure the CPD between the semiconductor surface and a vibrating reference Au probe, whose work function, Φ_M, is assumed to be constant. The shift of the Fermi level (E_f) of the semiconductor surface (i.e. the change in Φ_{SC}, the semiconductor work function) due to ligand adsorption was calculated from changes in CPD measurements in the dark:

$$\Delta CPD = \Delta(\Phi_{SC} - \Phi_M) = \Delta\Phi_{SC}$$

The change in work function, $\Delta\Phi_{SC}$, can be due to a change in electron affinity, $\Delta\chi$, and/or a change in band bending, ΔV_{bb}:

$$\Delta\Phi_{SC} = \Delta\chi \pm \Delta V_{bb} \qquad (+\text{ for n-type; }-\text{ for p-type})$$

From CPD measurements under illumination, the band bending, V_{bb}, can be estimated, before and after adsorption. Consequently, the contribution of the change in band bending, ΔV_{bb}, and of the change in the electron affinity, $\Delta\chi$, to the work function change of the semiconductor, $\Delta\Phi_{SC}$, can be calculated.

We measured the CPD (in the dark and under illumination) of the semiconductor before and after ligand adsorption. To check that the CPD changes were due to bound rather than excess ligand on the surface, we rinsed the sample with a 1 mM acetonitrile solution of ligand (after the initial immersion in 5 mM ligand in acetonitrile and subsequent CPD measurement), quickly dried the sample, and again measured the CPD. If the CPD values of the crystalline sample differed by more than 35 mV after the 5 and 1 mM treatments, the measurement was rejected. All experiments were repeated at least twice, thus giving at least four values for each measurement (two at 5 mM and two at 1 mM). The CPD values on the polycrystalline films vary over a wider range (±100 mV) than do single crystals values (±50 mV). This is reasonable, considering the polycrystalline surface morphology of these films. After a few minutes for stabilization, CPD values on single crystals are generally stable for 5–60 min (drifts less than 50 mV). Both control and ligand-treated samples do, however, show CPD drifts over longer periods of time.

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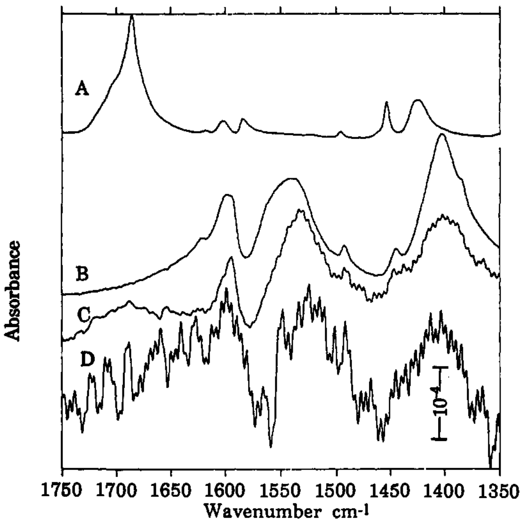

Figure 1. FTIR spectra of (A) benzoic acid in KBr, (B) cadmium benzoate in KBr, (C) a benzoic acid treated CdTe ATR plate (smoothed), and (D) a CdTe single crystal treated with benzoic acid (smoothed). Absorbance bar is for spectrum D only. Other spectra have been scaled down.

FTIR Measurements. FTIR spectra (Bruker IFS66) of the intrinsic single crystals of CdTe were measured in the transmission mode. FTIR spectra of the polycrystalline films were obtained using a grazing angle reflectance attachment (80° angle of incidence). To attain higher signal-to-noise ratios on the $CuInSe_2$ thin film, a mercury–cadmium telluride detector was used along with polarized light (*E* vector perpendicular to the surface).

The spectrum of the etched sample before adsorption was used as the background spectrum. The attenuated total reflectance (ATR) technique was used, with parallelepiped shaped CdTe substrates to achieve a better signal-to-noise ratio and confirm the single crystal spectra. Some of the ATR and transmission spectra had to be smoothed to remove a high frequency, sinusoidal noise which we attribute to interference patterns due to variations in crystal thickness or position.

Adsorption Isotherms. The adsorption isotherm of benzoic acid on the CdTe ATR plate was derived from FTIR absorption data. The surface benzoate absorption at 1595 cm^{-1} was assumed to be proportional to the amount of benzoate on the surface and was converted into surface coverage (number of monolayers) using a calibration with sodium benzoate as described in the Results and Discussion. The isotherm was created by running the experiment at several benzoic acid concentrations and recording the absorbance. The isotherm presented is an average of two experiments.

The adsorption isotherm of benzoic acid on CdTe powder was derived from UV/vis absorbance spectra. A 500-mg sample of powder was mixed with a known amount of benzoic acid in 1 mL of acetonitrile. The mixture was then centrifuged, and the absorbance of benzoic acid in the supernatant solution was measured. The amount of ligand on the powder was obtained by subtracting the amount of ligand remaining in the supernatant from the original amount of ligand. Surface coverage was obtained by dividing the amount of adsorbed ligand by the number of moles calculated to give a surface coverage of one monolayer (the calculated surface area of the powder being 1000 cm^2/g). We followed this procedure for several concentrations of ligand. The isotherm presented is an average of two experiments.

Results and Discussion

In this section, we aim at establishing the occurrence and mode of surface binding of both families of compounds, benzoic acids and benzohydroxamic acids, using FTIR spectroscopy and at providing an estimate for surface coverage from infrared absorption intensities. We then evaluate the electronic consequences of surface binding using the results of CPD measurements and establish the nature of the changes by comparing such measurements in the dark with those under illumination. We correlate the electronic effects with the character of the ligands, as expressed by their dipole moments.

Table 1. FTIR Frequencies (cm^{-1}) of Benzoic Acid Derivatives ($R-C_6H_4-COOH$) Adsorbed on CdTe ATR Substrates

p-substituent, R	aromatic ring vibrations	COO^- asymmetric stretch	COO^- symmetric stretch
NO_2	not present	1560 ± 6	1411 ± 6
CN	1586 ± 4	1536 ± 6	1401 ± 6
Br	1589 ± 4	1535 ± 6	1401 ± 6
F	1605 ± 4	1532 ± 6	1403 ± 6
H	1595 ± 4	1541 ± 6	1398 ± 6
i-Pr	1589 ± 4 (weak)	1529 ± 6	1401 ± 6
OCH_3	1605 ± 4	1510 ± 6	1395 ± 6

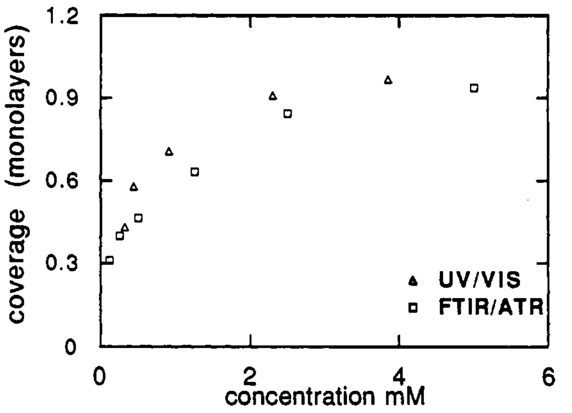

Figure 2. Adsorption isotherms of benzoic acid on CdTe powder (▲) obtained from UV/vis spectroscopy and on a CdTe ATR plate (□) obtained from FTIR spectroscopy, as described in the Experimental Section.

Adsorption of Benzoic Acids, FTIR. Figure 1 shows FTIR spectra of adsorbed benzoic acid on a CdTe single crystal and on an ATR substrate along with spectra of benzoic acid and cadmium benzoate in a KBr pellet. The carbonyl frequency (1687 cm^{-1}) is replaced by the carboxylate frequencies[36,37] (1530 and 1400 cm^{-1}) upon adsorption of benzoic acids on CdTe. This is in agreement with the change occurring when benzoic acid is bound to Cd(II) in cadmium benzoate. Similar shifts occur when carboxylic acids bind to other metal-containing surfaces.[29,37-39] We conclude that the adsorbed species are Cd-coordinated benzoates. All benzoic acid derivatives that were examined gave similar spectra on CdTe. Table 1 gives peak positions of these spectra between 1800 and 1300 cm^{-1}. The splitting $\Delta\nu$ between the carboxylate symmetric and the asymmetric stretch vibration (see Table 1) suggests that the coordination to Cd is bridging.[40]

Surface Saturation, Adsorption Isotherms. Figure 2 shows adsorption isotherms of benzoic acid on a CdTe ATR substrate and on CdTe powder. The powder isotherm is derived from UV/vis analysis of a solution after exposure to the powder. The ATR isotherm is derived from FTIR analysis of the amount of ligand adsorbed on the surface. Remarkably, and notwithstanding the basic differences in experimental observables used by the two methods, the isotherms are virtually identical. This agreement is strong evidence for the validity of the results, especially in view of the fact that the powders and the ATR plate may expose

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(40) If the observed splitting ($\Delta\nu$) between the symmetric and asymmetric stretches is equal or nearly equal to that of the purely ionic salt (sodium benzoate, 142.5 cm^{-1}), the coordination is regarded as ionic. If the splitting is much smaller than in an ionic compound, it is regarded as bidentate, and when $\Delta\nu$ takes a value between the values for ionic and bidentate structures, the coordination is regarded as bridging. Unidentate complexes show $\Delta\nu$ values much greater than those of ionic complexes (around 200 cm^{-1}). The difference between bridging and bidentate is not as clear cut as that in the other cases (ref 32): Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley & Sons: New York, 1986; pp 232. Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227–250.

different distributions of crystal faces. The isotherms suggest that a 5 mM concentration of benzoic acid is sufficient to saturate the surface on both the powder and the ATR substrate. We cannot be absolutely certain that the surface is saturated, however, because this experiment cannot be performed at ligand concentrations of >0.01 M. At high ligand concentrations, excess unbound ligand collects on the surface and obscures binding peaks.

Surface Coverage. We used FTIR absorption data to assess the surface coverage. We calculated the amount of benzoic acid needed to cover the ATR substrate with one monolayer and spread a solution containing this amount of sodium benzoate on the substrate. The solvent evaporated, and the subsequent FTIR absorbance at 1595 cm^{-1} was measured. By taking this value as the absorbance of one monolayer and by determining a few more values for absorbance of fractions of a monolayer, we obtained a calibration curve which was essentially linear. Using this calibration, the amount of benzoic acid on the surface after adsorption is about 1.0 monolayer.

To calculate the amount of benzoic acid in a monolayer, we assumed a flat surface and a surface area of 25 Å^2 per benzoic acid molecule. This is a reasonable estimate for the surface area occupied by a molecule containing a benzene ring,[41] but the area may increase somewhat if the molecule is highly tilted from the surface normal. To check surface roughness, we performed SEM investigations which showed that the surface roughness of the ATR plate is less than 2. Atomic force microscopy on the etched single crystals also suggested a surface roughness less than 2. Thus, within a factor of 2–3, the saturated surface is covered with a monolayer of benzoic acid.

The same method cannot be used to convert IR transmission data to surface coverage on single crystals because the area is too small and the solvent does not evaporate uniformly. In this case we used a solution spectrum of sodium benzoate as a calibration. A 5×10^{-4} M solution of sodium benzoate in dimethyl sulfoxide gives an absorbance of 0.0055 at the vibration frequency of the carboxylate asymmetric stretch. With a cell length of 0.2 mm and a 5×10^{-4} M concentration, we calculated that 6.0×10^{15} molecules/cm^2 are encountered by the IR beam. On a crystal covered by a monolayer in which one benzoic acid molecule occupies 25 Å^2, there are 8×10^{14} molecules/cm^2 (remembering that both sides of the single crystal are exposed in the transmission experiment). The absorbance of the carboxylate asymmetric stretch of benzoate on the CdTe single crystal is 0.00025, which would correspond to 0.34 monolayers. Using peak areas instead of peak heights, however, gives a value of about 0.9 monolayers. Thus, to a rough approximation, the surface coverage on the single crystal is the same as that on the ATR crystal, i.e. on the order of 1 monolayer. If the benzoic acid on the surface is somewhat tilted, molecules will take up more area and monolayer coverage will be slightly less than 1, as we observe.

Adsorption of Benzohydroxamic Acids on CdTe Single Crystals, FTIR. Figure 3 (top) presents the IR spectra of DPH adsorbed on single crystal CdTe. The spectrum of the adsorbed species resembles the spectrum of the Cd(DPH)$_2$ complex in KBr very closely and not that of uncomplexed excess DPH on the crystal, showing that the hydroxamic acid is adsorbed as a hydroxamate–Cd complex. The spectrum of excess DPH on the crystal closely resembles the spectrum (not shown) of DPH in KBr (within 5 cm^{-1}). We show two methods of DPH adsorption: (a) letting a solution of DPH evaporate on the surface of CdTe and subsequent rinsing off of unbound DPH and (b) immersing CdTe in a 5 mM solution of DPH and dabbing the crystal dry. Although the former method gives larger, more reproducible FTIR peaks, it may result in more than 1 monolayer of DPH on the surface. This is why we prefer adsorption from a 5 mM solution for the CPD experiments.

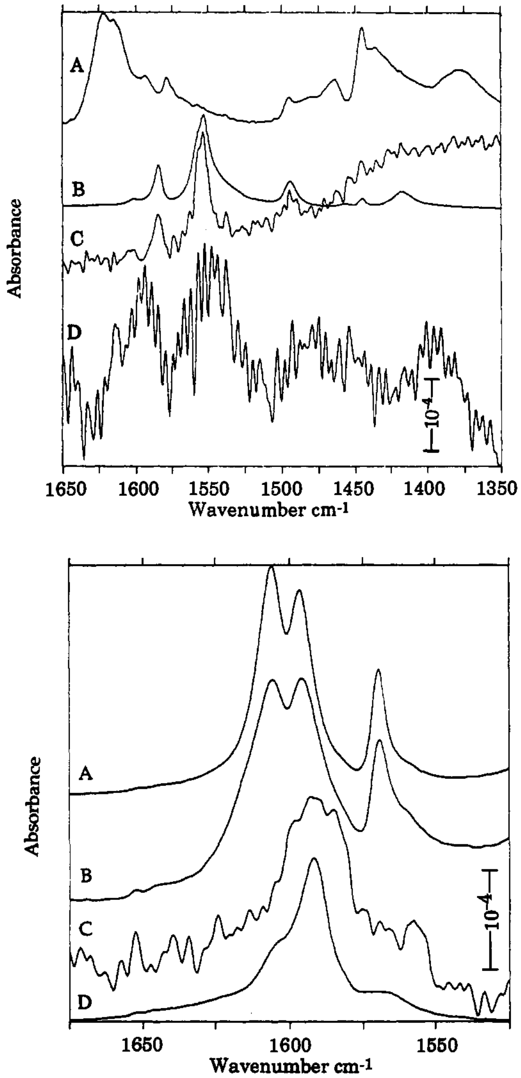

Figure 3. (top) FTIR spectra of (A) excess DPH on a CdTe single crystal (a 5 mM solution of DPH in CH$_3$CN was allowed to evaporate on the crystal), (B) Cd(DPH)$_2$ in KBr, (C) DPH on a CdTe single crystal (treated as in A and then rinsed with 2 mL of CH$_3$CN), and (D) DPH on a CdTe single crystal (immersion in a 5 mM solution followed by dabbing dry). Absorbance bar is for spectrum D only. Other spectra have been scaled down. (Bottom) FTIR spectra of (A) *p*-CH$_3$SO$_2$-*N*-methylbenzohydroxamic acid (L) in KBr, (B) excess L on a CdTe single crystal (C) L adsorbed on a CdTe single crystal, and (D) the CdL complex in KBr. Absorbance bar is for spectrum C only. Other spectra have been scaled down.

Interpreting the spectra of adsorbed *N*-methylbenzohydroxamic acids is unfortunately not as simple as that for DPH. The FTIR spectra of adsorbed *p*-(methylsulfonyl)-*N*-methylbenzohydroxamic acid together with the KBr spectra of the respective free ligand and its Cd complex are shown in Figure 3 (bottom). Note that the spectrum of excess free ligand (precipitated) on the crystal is similar to that of the free ligand in KBr. The spectrum of the adsorbed ligand, however, resembles that of the approximately 1:1 Cd–ligand complex in KBr. The fact that the carbonyl shift between the free ligand and its complex is small is attributed to extensive hydrogen bonding of the free ligand, which reduces the carbonyl group's double bond character prior to metal binding.

Adsorption of Benzohydroxamic Acids on Thin Films, FTIR. Figure 4 presents the FTIR spectra of DPH adsorbed on polycrystalline films of CdTe (Figure 4 (top)) and CuInSe$_2$ (Figure 4 (bottom)), along with the spectra of DPH and the Cd and In complexes of DPH in a KBr pellet. DPH on CdTe has absorption peaks at 1585 and 1559 cm^{-1}, and the spectrum of DPH adsorbed on CuInSe$_2$ has peaks at 1589 and 1539 cm^{-1}. The peak around

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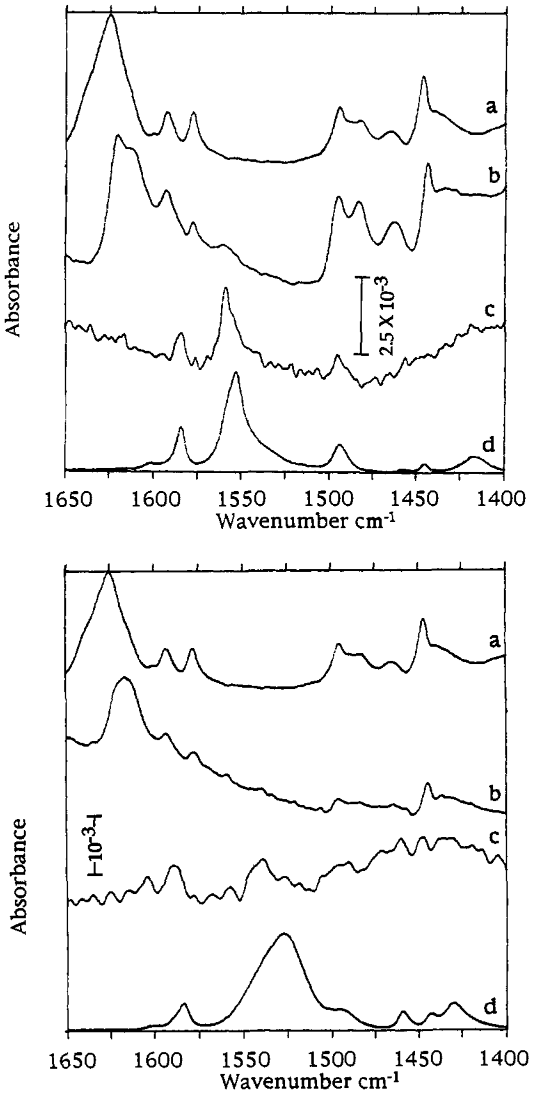

Figure 4. (top) FTIR spectra of (a) DPH in KBr and (d) $Cd(DPH)_2$ in KBr. Grazing angle reflectance FTIR spectra of (b) excess DPH on a CdTe polycrystalline film (allowing a solution to evaporate on the film) and (c) sample b rinsed with 1 mL of 5 mM DPH in acetonitrile (see the Experimental Section). Absorbance bar is for spectrum c only. Other spectra have been reduced. (bottom) FTIR spectra of (a) DPH in KBr and (d) $In(DPH)_3$ in KBr. Grazing angle reflectance FTIR spectra of (b) excess DPH on a polycrystalline $CuInSe_2$ film (allowing a solution to evaporate on the film) and (c) sample b rinsed several times with 1 mL of 1 mM DPH in acetonitrile (see the Experimental Section). Absorbance bar is for spectrum c only. Other spectra have been reduced.

1587 cm^{-1} was assigned to the carbonyl vibration[33] upon metal complexation. The absorption maxima on the thin films are close (within 10 cm^{-1}) to the corresponding peaks in the metal–DPH complex spectra. Therefore, we conclude that DPH adsorbs on a CdTe polycrystalline film as a Cd–DPH complex and on a $CuInSe_2$ polycrystalline film as an In–DPH complex.

Single Crystal CPD Measurements. CPDs were measured on CdTe single crystals before and after adsorption of benzoic and benzohydroxamic acids. The CPD measurements in the dark on intrinsic CdTe crystals showed that the change in the semiconductor's surface potential varies linearly with the Hammett parameters of the substituents of the adsorbed benzoic acid (except for *p*-fluorobenzoic acid) as shown in Figure 5. A similar correlation exists with the dipole moments of the corresponding substituted benzenes. Both the Hammett parameter and dipole moment reflect the electron withdrawing or donating power of the substituent. Similar results were obtained on single crystals of *n*-CdTe where *p*-NO_2, *p*-H, and *p*-OCH_3 gave shifts in the surface potential of 360 ± 80, –40 ± 10, and –140 ± 20 mV, respectively.

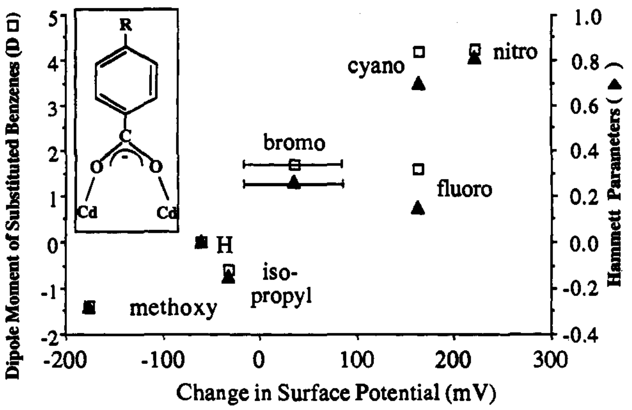

Figure 5. Surface potential of an intrinsic CdTe single crystal as a function of the Hammett parameters[56,58] of the adsorbed benzoic acids' substituents and of the dipole moments of the corresponding substituted benzenes.[46] For clarity, the error bar, which represents the highest observed standard deviation of four measurements for any of the derivatives, is shown only for the bromo derivative. The insert is a schematic drawing of a benzoic acid derivative binding to the metal of a semiconductor surface in a bridging configuration.

Table 2. Changes in Contact Potential Difference (mV) upon Adsorption of Several Substituted *N*-Methylbenzohydroxamic Acids ($R-C_6H_4-CON(OH)CH_3$) on Single Crystal CdTe

para substituent, R	Hammett parameter[56,57]	CPD change on n-CdTe	CPD change on intrinsic CdTe
NO_2	0.81	230 ± 80	290 ± 10
CH_3SO_2	0.72	–30 ± 70	20 ± 20
H	0.00	–230 ± 10	–260 ± 40
OCH_3	–0.28	–330 ± 20	–280 ± 20

The *N*-methylbenzohydroxamic acid derivatives showed the same dependence of CPD on the Hammett parameter (Table 2). Note again the large changes of surface potential due to treatment with different ligands. These results indicate that the direction and the magnitude of the ligand's dipole moment control the semiconductor's work function. We note that large surface potential changes were also observed for Langmuir–Blodgett films of alkanoic acids and adsorbed films of perfluoroalkanoic acids on GaP.[42,43] Very large changes in flat band potential as a result of electrochemical oxidation/reduction of CdTe and $CuInSe_2$ have also been observed.[44,45] In none of these cases were the results interpreted as being due to a dipole layer at the surface.

A simple calculation shows that a 500-mV change in surface potential can be due easily to the dipole moment of the ligand. The difference between the dipole moments of the *p*-OCH_3 and the *p*-NO_2 benzene derivatives is 5.6 D.[46] Assuming that the changes in CPD introduced by these molecules are due to their dipole moments, we can calculate the expected change in surface potential that these molecules induce. The potential drop, ΔV, due to a dipole layer is given by

$$\Delta V = \mu \cos \Theta / \epsilon \epsilon_0$$

where μ is the dipole moment per area, Θ is the angle between the dipole and the surface normal, ϵ is the dielectric constant, and ϵ_0 is the permittivity of free space.[47] Assuming that the surface contains a monolayer of ligand, the density of dipoles is about 1

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Table 3. Changes in Contact Potential Difference (mV) upon Adsorption of Several Substituted *N*-Methylbenzohydroxamic Acids (R-C_6H_4-CON(OH)CH_3) on CdTe and $CuInSe_2$ Polycrystalline Films

para substituent, R	Hammett parameter[56]	CPD change in CdTe film	CPD change in $CuInSe_2$ film
NO_2	0.81	380 ± 50	340 ± 40
H	0.00	−220 ± 40	−200 ± 50
OCH_3	−0.28	−290 ± 90	−260 ± 80

dipole per 25 Å^2. Using the dielectric constant of 5.3 suggested for aromatic molecules in monolayers,[48,49] the expected potential difference is 1.6 V, if the molecules were oriented vertically. This suggests that, if we have a monolayer of molecules, they are highly tilted. High tilts are also suggested by the presence of both the symmetric and asymmetric stretches in the IR spectrum. For vertically oriented molecules, the symmetric stretch is usually very weak in the ATR mode.[29] It is also possible that the coverage is a factor of 2 or 3 less than that of an ideal monolayer (see the section on surface coverage).

Thin Film CPD Measurements. CPD measurements on polycrystalline CdTe[50,51] and $CuInSe_2$[30] films used for state of the art solar cell fabrication show similar changes in surface potential upon treatment with the hydroxamic acid derivatives. (See Table 3.) The fact that the treatment also works on $CuInSe_2$ shows that it can be extended to other semiconductors.

As described in the Experimental Section, the overall change in surface potential (work function) of a semiconductor is equal to the sum of changes in band bending and electron affinity. The presence of a dipole layer affects only the electron affinity.[52] However, if the ligand interacts with the surface so as to change the density of surface states, then the band bending in the semiconductor may also change. We estimated the band bending by measuring the difference between CPD in the dark and under strong white illumination (≈1 W). Upon ligand adsorption, we observed changes of less than 50 mV in band bending, as compared to control experiments. Therefore, we can conclude that the carboxylate and the hydroxamate do not seem to affect significantly the surface state density. It has been shown previously that some ligands affect the photoluminescence intensity of CdSe and GaAs.[17-24] The results for CdSe were rationalized as a change in the width of the dead layer implying changes in band bending, although other explanations are possible.[24] In view of the fact that we have not yet found significant changes in band bending with the ligands used, we are exploring other modifications of the ligands and their mode of adsorption so as to change the band bending of CdTe or $CuInSe_2$.

Competition of Adsorption between Benzohydroxamic Acids and Benzoic Acids. In an attempt to trace the factors that affect ligand binding, CdTe was exposed to mixtures of benzoic acid and hydroxamic acid derivatives and the predominantly bound ligand was established by CPD measurements. Thus, treatment of CdTe with an equimolar mixture of *p*-methoxybenzoic acid and *p*-nitro-*N*-methylbenzohydroxamic acid increased the CPD by 100 mV, suggesting predominant binding of the hydroxamate. Similarly, exposure of CdTe to an equimolar mixture of *p*-nitrobenzoic and *p*-methoxy-*N*-methylbenzohydroxamic acids increased the CPD by 150 mV, demonstrating predominant binding of the benzoic acid.[53] The preferred binding of the *p*-nitro derivatives, independent of the nature of the binding group, suggests that the ease of proton dissociation controls the efficacy of surface binding.

Conclusions

FTIR spectra of benzoic and hydroxamic acid molecules adsorbed on CdTe single crystals and hydroxamic acids on photovoltaic quality CdTe and $CuInSe_2$ polycrystalline thin films show that, upon adsorption, the molecules bind to In in the case of $CuInSe_2$ and to Cd in the case of CdTe. In the latter case, benzoic acids probably bind to Cd on CdTe in a bridging geometry. CPD measurements show that adsorption of molecules of these families of organic compounds changes the work function of these semiconductors. The changes in work function are found to be due to changes in the semiconductors electron affinities. The direction and magnitude of these changes can be controlled by substitution of polar functional groups on the phenyl ring of the benzoic acid or benzohydroxamic acids. The changes correlate well with the dipole moments of the substituted phenyl part and with the Hammett parameters of the substituent groups. They can be accounted for by the cooperative effect of the molecular dipoles of the adsorbed ligands, in creating an additional capacitance on the surface. The extent of the variations in electron affinity, effected in this way, is rather large. Thus, with hydroxamic acids, a range of 550 mV is spanned on single crystal CdTe, 600 mV on $CuInSe_2$ films, and up to 670 mV on CdTe thin films. In the case of $CuInSe_2$, this is more than half of the band gap value.

The fact that we were able to obtain results with two families of organic compounds that differ in their chelating groups and on two types of chalcogenide semiconductors suggests that we are dealing with a phenomenon of a general nature. The application of the procedure described here to polycrystalline films of the type used in solar cells may be promising for future applications if the results of the procedure are sufficiently stable. In this respect, we note that benzoic acids remain intact and adsorbed on MnO_2 at 575 K in vacuum.[37] We find hydroxamates to be stable when adsorbed on CdTe and $CuInSe_2$ in a 10^{-9} Torr vacuum. Therefore, the use of organic ligands for band edge engineering[54] appears to be a realistic possibility.

In the systems described here, changes in electron affinity dominate the measured changes in work function, i.e. there are no measurable changes in band bending. This may well be due to Fermi level pinning.[55] We are currently working on finding molecular parameters that will affect band bending as well. Control of both band bending and electron affinity would constitute full control over the semiconductor surface. A further challenge we are exploring is to show that surface potential changes, induced by organic ligand binding, can modify actual charge transport close to or across semiconductor surfaces.

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