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Controlling the Work Function of CdSe by Chemisorption of Benzoic Acid Derivatives and Chemical Etching

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Fourier transform infrared spectroscopy shows that benzoic acid and its derivatives can bind chemically to the surfaces of CdSe. The dipole moment of the adsorbed benzoate correlates linearly with changes in the semiconductor work function, as determined by vibrating capacitor (Kelvin probe) measurements. Because ligand adsorption does not induce significant changes in surface photovoltage, we conclude that changes in work function are due to changes in electron affinity rather than in band bending. This means that ligand adsorption does not induce charge transfer between the surface and the semiconductor but rather adds a surface dipole. Changes in band bending do occur, however, upon conventional etching.

Introduction

Control over the surface and interface chemistry and physics of semiconductors is essential for constructing semiconductor devices and for fine tuning their electrical performance. Critical parameters for such control are the electron affinity, i.e., the energy difference between the bottom of the conduction band at the surface and the vacuum level, and the built-in potential. (See Figure 1.) The latter is due to the electric field near the surface (the space charge layer) and is expressed in the electron energy band diagram as band bending at the surface. The electron affinity is directly affected by any surface dipole.¹ On this basis, we developed ways for chemical modification of the surface of some semiconductors, using adsorption of polar organic ligands. This allowed us to use the tunability of the ligands' dipole moments to control the electron affinity, and consequently the surface potential (work function), of the modified semiconductor. Ideally we would like to control independently both electron affinity and band bending at the semiconductor surface.

Earlier we reported that the work functions of CdTe and CuInSe₂ single crystals and polycrystalline thin films vary with the dipole moment of adsorbed benzoic and hydroxamic acid derivatives.² By comparing contact potential differences obtained in the dark with those obtained under strong illumination (photosaturation technique), we concluded that the adsorbate-induced surface potential changes are the result of changes in electron affinity rather than in band bending.

On GaAs, organic ligand-induced photoluminescence (PL) changes were attributed to changes in both surface recombination velocity and band bending.^{3,4} On the wider band gap semiconductor, CdSe, PL data that were obtained after adsorption of several series of organic molecules were interpreted in terms of changes in band bending.^{5–10} On the basis of those literature data and our earlier results, we set out to investigate the effect of the adsorption of benzoic acid derivatives on CdSe. In addition we investigated the effect of *p*-methoxy- and *p*-cyanoaniline adsorption on CdSe to see the band bending changes that were suggested by solution PL measurements on those systems.⁸ As part of these investigations, we checked

the effects of etches on the work function, band bending, and surface composition of CdSe.

Experimental Section

Materials. Single crystals of (0001) oriented n-CdSe ($\rho = 3 \Omega \cdot \text{cm}$) were purchased from Cleveland Crystals. Benzoic acid derivatives were used as received. Solutions of benzoic acids were prepared in acetonitrile (HPLC grade). *p*-Methoxyaniline was purified by sublimation, and *p*-cyanoaniline (Aldrich) was used as received from a freshly opened bottle. Solutions of aniline derivatives were prepared in toluene (analytical grade) through which nitrogen was bubbled. These solutions were used immediately, with nitrogen bubbling throughout the experiment.

Crystal Treatments. The Cd and Se faces were distinguished by etching in Br₂/methanol (2 min in 1% (v/v) or 5 s in 3.3% (v/v), followed by a methanol rinse). These etches usually reveal the shiny Cd (A) face (0001) and the dull Se (B) face (000 $\bar{1}$), but the distinction between faces is not always clear.^{8,11,12} Crystals were initially polished with pastes of 5, 1, and 0.3 μm diameter alumina particles. Prior to each experiment, the CdSe crystal was polished with 0.05 μm diameter alumina paste, immersed in boiling methanol for several minutes, again polished with 0.05 μm diameter alumina paste, and etched by one of the Br₂/methanol treatments given above. In some cases the 1% Br₂/methanol etch was followed by a 15-min etch in 100% hydrazine hydrate and subsequent rinses in methanol and deionized water. To adsorb benzoic acid derivatives on CdSe, we immersed the etched crystal 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.

FTIR Measurements. FTIR spectra (Bruker IFS66) of benzoic acid derivatives adsorbed on single crystals were measured in the transmission mode, using a DTGS detector. The spectrum of the same etched sample before ligand adsorption was used as background. Such measurements show that there is little unbound ligand on the surface.

XPS Measurements. X-ray photoelectron spectra were obtained using Al K α X-radiation on a Kratos Axis-HS instrument. Samples were prepared by Br₂/methanol (1% (v/v)) and hydrazine etches as described above and loaded into the vacuum chamber approximately 30 min after etching. Spectra were recorded before and after Ar plasma sputtering

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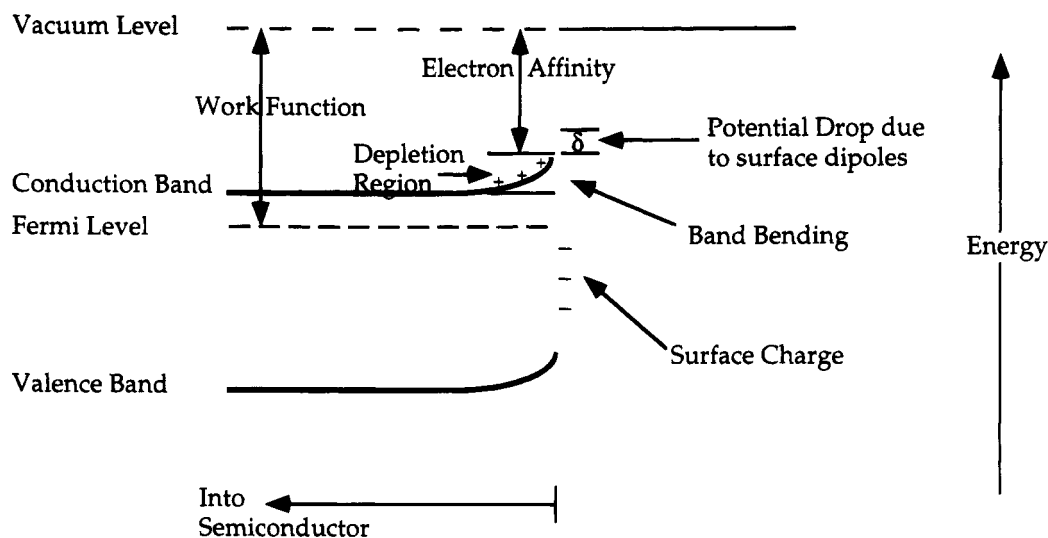


Figure 1. Schematic band diagram of a semiconductor surface with band bending and surface dipoles.

on the Cd face of the samples using a pass energy of 20 eV. The Cd 3d photoelectron line of CdSe was used as a standard (binding energy of 405.0 eV¹³), and binding energies were corrected for charging accordingly.

Contact Potential Difference Measurements. Kelvin probe measurements were performed in air on a commercial instrument (Delta Phi Besocke, Jülich, Germany). Even though the method has been described elsewhere,¹⁴ its importance to the experiments that we report on here justifies some explanation. The Kelvin probe measures the contact potential difference (CPD), the energy difference between the work function of the sample and that of the vibrating reference metal electrode. In the dark, the change in CPD, ΔCPD , due to ligand adsorption is equal to the change in the sample's work function according to

$$\Delta\text{CPD} = \Delta(\Phi_{\text{SC}} - \Phi_{\text{M}}) = \Delta\Phi_{\text{SC}} \quad (1)$$

where Φ_{SC} is the semiconductor's work function and Φ_{M} is the work function of the metal (reference electrode). The shift in the Fermi level of the sample with respect to the vacuum level (change in work function) can be due to a change in electron affinity, a change in band bending, or a combination of these two (see Figure 1).

To check that CPD changes were due to bound rather than excess free 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 sample after the 5 and 1 mM treatments differed by more than 40 mV, the measurement was rejected. In one case, *p*-nitrobenzoic acid on a 1% Br₂/methanol treated surface, the minimum CPD difference between 5 and 1 mM treatments was 60 mV. This may be due to removal of a small amount of selenium during the treatment (see Results and Discussion, on XPS). After a few minutes for stabilization, CPD values are stable for at least 15 min (drifts less than 50 mV). After an overnight period, however, some CPD changes drifted to about 50% of their initial value. This drift might be due to evaporation of solvent and consequent reorganization of the ligand layer, but other explanations are possible. We have recently found that adsorbate-induced work function changes on gold films endure for periods from days to weeks (Bruening et al. To be published).

Photosaturation Measurements. Upon illumination of the semiconductor (light with $h\nu > E_{\text{G}}$, the band gap of the semiconductor) electron-hole pairs are created. These can

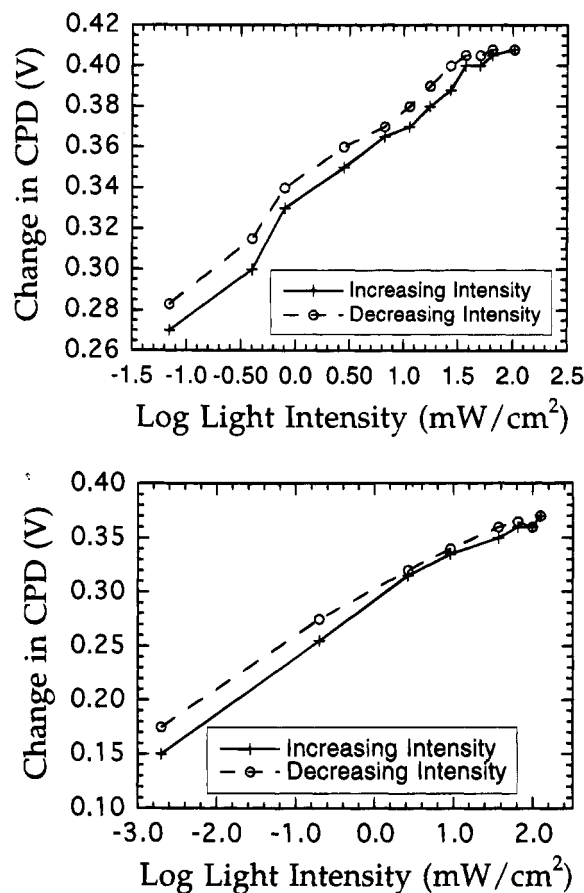


Figure 2. (a) Change in contact potential difference of a CdSe crystal versus intensity of white illumination. The illumination source was a 300 W halogen lamp with an IR filter, and intensity was controlled using a variable voltage source. The crystal was etched for 2 min in 1% Br₂/methanol. (b) Change in contact potential difference of a CdSe crystal versus intensity of Ar⁺ laser (514.5-nm) illumination. The illumination intensity was controlled using optical density filters. The crystal was etched for 2 min in 1% Br₂/methanol.

migrate under the influence of the electric field that exists in the space charge layer, so as to decrease the space charge and thus the band bending. Thus, the difference between CPD values in the dark and under strong illumination (photosaturation) gives an estimate of initial band bending. A plot of surface potential versus light intensity (300 W halogen lamp) on a semilog plot (Figure 2a) suggests that the intensity used in band

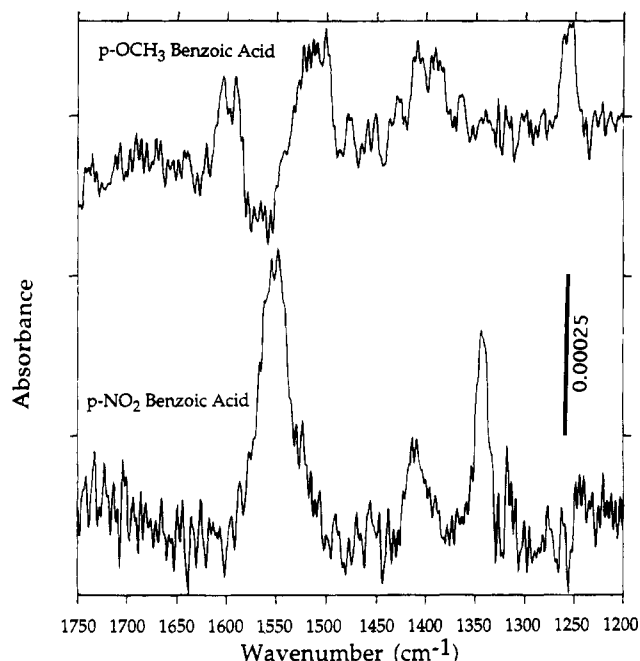


Figure 3. FTIR spectra of *p*-methoxy- and *p*-nitrobenzoic acid adsorbed on a CdSe single crystal. Spectra were measured in the transmission mode using the same etched crystal without ligand as a background.

bending measurements, 50 mW/cm², is sufficient for neutralizing the space charge, i.e., for flattening the bands so that the remaining band bending is less than 50 mV. This can be seen because the plot deviates from linearity at high light intensities.^{15,16} As an additional check that the bands were basically flat at the surface, we measured CPD versus light intensity using an Ar⁺ laser, which gives more controlled (constant wavelength, 514.5-nm) radiation. The data under laser illumination (shown in Figure 2b) again suggest that the bands are nearly flat (remaining band bending of less than 50 mV) at intensities greater than 50 mW/cm². If the intensity of the laser is increased even more, then sharp changes in CPD occur again. We attribute this to chemical reactions at the surface, the study of which is beyond the scope of this paper.

Although photosaturation is an established technique,^{15–20} recent work on the measurement of quasi-Fermi levels²¹ evoked discussion as to whether or not photosaturation measurements are affected by these levels. This question can be answered by taking into consideration two facts. (1) For sufficiently thick samples and/or sufficiently short illumination wavelengths, the bulk contains no photogenerated carriers. These carriers, which are only generated near the surface, recombine before reaching the bulk of the sample. (2) No net current flows through the sample in a Kelvin probe measurement. Thus, in the illumination-affected region, currents due to photogenerated electrons and holes are equal in magnitude but opposite in sign. If mobilities of electrons and holes were the same, no electric field would be needed to keep hole and electron currents of equal magnitude. In fact electron and hole mobilities are somewhat different and a Dember voltage does arise, but this voltage is negligibly small.^{15,16} If no fields are present between the bulk and the illuminated semiconductor region, then the electrons in the illuminated region have the same overall electrochemical potential as the bulk. Furthermore, from (1) above, there is no separate effect of illumination on the bulk electrochemical potential. Because this potential is the measured variable in Kelvin probe measurements, formation of quasi-Fermi levels does not affect the measurements.

TABLE 1: Changes in Surface Potential and Band Bending of CdSe after Several Etching Procedures

treatment	crystal face (0001)	change in surface potential ^b (mV)	band bending (mV)
polishing only	Cd	0 ± 10	170 ± 30
1:30 Br ₂ /MeOH	Cd	700 ± 40	500 ± 10
1:30 Br ₂ /MeOH	Se	550 ± 75	450 ± 30
1:100 Br ₂ /MeOH	Cd	630 ± 50	450 ± 40
1:100 Br ₂ /MeOH	Se	520 ± 20	410 ± 20
100% hydrazine hydrate ^a	Cd	300 ± 40	450 ± 10
100% hydrazine hydrate ^a	Se	220 ± 30	420 ± 10

^a The hydrazine etch followed a 1% Br₂/methanol etch. See Experimental Section for details. ^b With respect to the polished Cd face of the crystal.

TABLE 2: Ratio of Cd to Se (Atomic) after Several Surface Treatments As Determined from XPS Measurements

surface treatment	ratio of Cd to Se ^a
1:100 Br ₂ /MeOH	0.4
100% hydrazine hydrate ^b	1.0
1:100 Br ₂ /MeOH plus sputtering	1.0
100% hydrazine hydrate ^b plus sputtering (used as a standard)	1.0

^a Estimated error ±0.05. ^b The hydrazine etch followed a 1% Br₂/methanol etch. See Experimental Section for details.

Results and Discussion

Adsorption of Benzoic Acid Derivatives FTIR. Figure 3 shows FTIR spectra measured through CdSe single crystals onto which *p*-nitro- and *p*-methoxybenzoic acids were adsorbed. The low signal to noise ratio is due to the fact that we are looking at ≈1 monolayer coverage in the transmission mode. The fact that the carbonyl peak of the free acid (1690 cm⁻¹) is absent indicates that the peaks are not due to precipitated, unbound benzoic acid. The symmetric (1550-, and ≈1510-cm⁻¹) and asymmetric (≈1410-cm⁻¹) stretches of the carboxylate are present, however.^{22,23} The symmetric stretches of the nitro and methoxy derivatives likely differ by ≈40 cm⁻¹ because of the electron withdrawing/donating properties of the nitro and methoxy groups.²⁴ The symmetric stretch of *p*-methoxybenzoic acid may also overlap with a mode of the aromatic ring.^{23b} The peak at 1345 cm⁻¹ in the *p*-nitrobenzoic acid spectrum is due to the nitro group.²⁵ We attribute the 1600-cm⁻¹ peak in the *p*-OCH₃ spectrum to an aromatic ring mode.²³ As was the case on CdTe, we do not see this ring mode in the adsorbed *p*-NO₂ derivative. The carboxylate stretches show that the molecules are deprotonated upon binding and that they are most likely binding to surface cadmium ions. These results are virtually identical to those that we reported earlier for CdTe single crystals and attenuated total reflectance (ATR) CdTe crystals.² (With the latter, the signal to noise ratios are much higher due to the multiple internal reflections possible in the ATR mode. ATR crystals made from CdSe are, unfortunately, not available.) The magnitudes of the absorbances due to adsorbed ligands suggest that coverage is approximately 1 monolayer.²

Surface Potential: Effect of Etching. Prior to ligand adsorption, the surface was polished and chemically etched. The chemical pretreatments themselves have a large effect on surface potential. Table 1 lists the changes in surface potential between a polished and an etched crystal. The Br₂/methanol treatment increases the work function as would be expected from an oxidizing etch (see the next section for chemical details). The hydrazine etch then reduces the work function as would be expected from a reducing treatment. The difficulty in preparing surfaces identically probably accounts for the large standard deviations in the values. The work function difference between

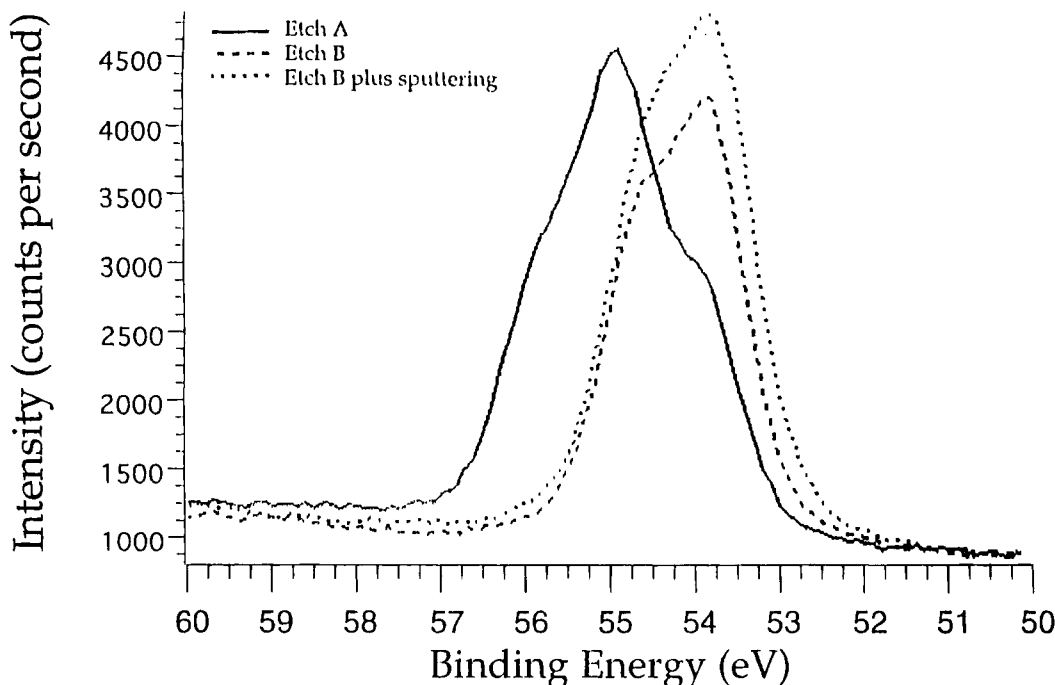


Figure 4. XPS spectra of CdSe after an etch in 1% Br₂/methanol (etch A), etch A followed by an etch in hydrazine (etch B), and etch B plus sputtering. See the Experimental Section for etching and measurement details.

the Cd (0001) and the Se(000 $\bar{1}$) faces is around 100 mV. The difference between the Cd and the Se faces agrees with previous studies on crystal polarity in CdTe.²⁶

XPS Measurements. Differences in work function due to different surface treatments should be reflected by differences in surface composition. XPS measurements showed that a Br₂/methanol etched CdSe crystal has elemental selenium on the surface as the product of oxidation. An additional hydrazine treatment left a stoichiometric surface, as shown in Table 2. The excess of selenium is also reflected in the shape and position of the Se 3d line, shown in Figure 4. After a Br₂/methanol etch the Se 3d line appears at a binding energy of 54.95 eV (the position of Se⁰²⁷) with a shoulder at \approx 53.9 eV, which corresponds to the binding energy of Se 3d in CdSe.²⁸ After sputtering or hydrazine etching, only the CdSe peak at 53.85 eV remains. This behavior is similar to that found for Te in CdTe after Br₂/methanol and hydrazine etches.²⁹ Because the work function of elemental selenium is higher than that of n-CdSe, it is not surprising that excess selenium increases the sample's work function. The work function of bromine/methanol treated samples decreases after immersion in toluene or acetonitrile. This probably reflects these solvents' ability to dissolve selenium.

Surface Potential: Effect of Adsorption. Figure 5 shows the relationship between the adsorbed ligands' dipole moment (alternatively, the substituent's Hammett parameter) and the surface potential of a CdSe crystal (hydrazine etched). As was the case with CdTe and CuInSe₂,² the surface potential of CdSe varies approximately linearly with ligand's dipole moment. The surface potential changes can be explained by the formation of a new capacitance on the semiconductor surface due to aligned ligand dipoles.

Treatment of CdSe with 3,5-dinitrobenzoic acid gave the largest surface potential change (510 mV) of any benzoic acid derivative. If the Hammett parameters of the two meta-substituents were additive, the overall Hammett parameter of the dinitrobenzoic acid would be 1.42 and its surface potential change should be 1.75 times that of *p*-nitrobenzoic acid.³⁰ The observed change is, however, only 1.2 times the change induced

by *p*-nitrobenzoic acid. The coverage of the 3,5-dinitro and *p*-nitro molecules as well as their dielectric constants could be different, so it is difficult to draw any firm conclusions concerning the additivity of the Hammett parameters. Adsorption of 3,5-dimethoxybenzoic acid caused surface potential changes of -110 mV. This result is reasonably consistent with a Hammett parameter of 0.2 for this molecule. (The Hammett parameter for a single *m*-OCH₃ substituent is 0.1.³⁰) The fact that the *m*-dimethoxy derivative gives less negative surface potential changes than the *p*-methoxy derivative reflects the difference between meta and para substituents.

Table 3 shows the differences between the surface potentials of *p*-methoxy- and *p*-nitrobenzoic acid treated crystals after two different etches and on the two polar crystal faces. The hydrazine etched Cd (0001) face shows the largest difference in surface potential. This can be understood by realizing that this face likely has more Cd sites for ligand binding.³¹ Both faces of Br₂/methanol etched crystals show surface potential changes which are slightly less than those obtained with the hydrazine etched Se face, suggesting a decrease in Cd sites upon Br₂/methanol etching, as was shown by XPS measurements.

Band Bending. Benzoic Acid Derivatives. The band bending changes induced by adsorption of benzoic acid derivatives are always less than 50 mV (relative to control experiments with only solvent). We have now seen this effect on CdTe, CuInSe₂, and CdSe. If the lack of band bending changes is due to Fermi level pinning, then the surfaces of both CdTe and the wider band gap material, CdSe, are pinned in air. In order to see if the hydrazine etch was responsible for the lack of band bending changes, we also looked for band bending changes due to ligand binding after a Br₂/methanol etch. Again no band bending changes greater than ± 50 mV occur. Thus, adsorption of benzoic acid derivatives on CdSe (and CdTe) allows control of electron affinity, independently of band bending.

Aniline Derivatives. Still, one would like to be able to control both the electron affinity and the band bending. Other researchers have shown that CdSe photoluminescence intensity varies linearly with the Hammett parameter of the substituents of adsorbed aniline derivatives.⁸ Such variation can be due to

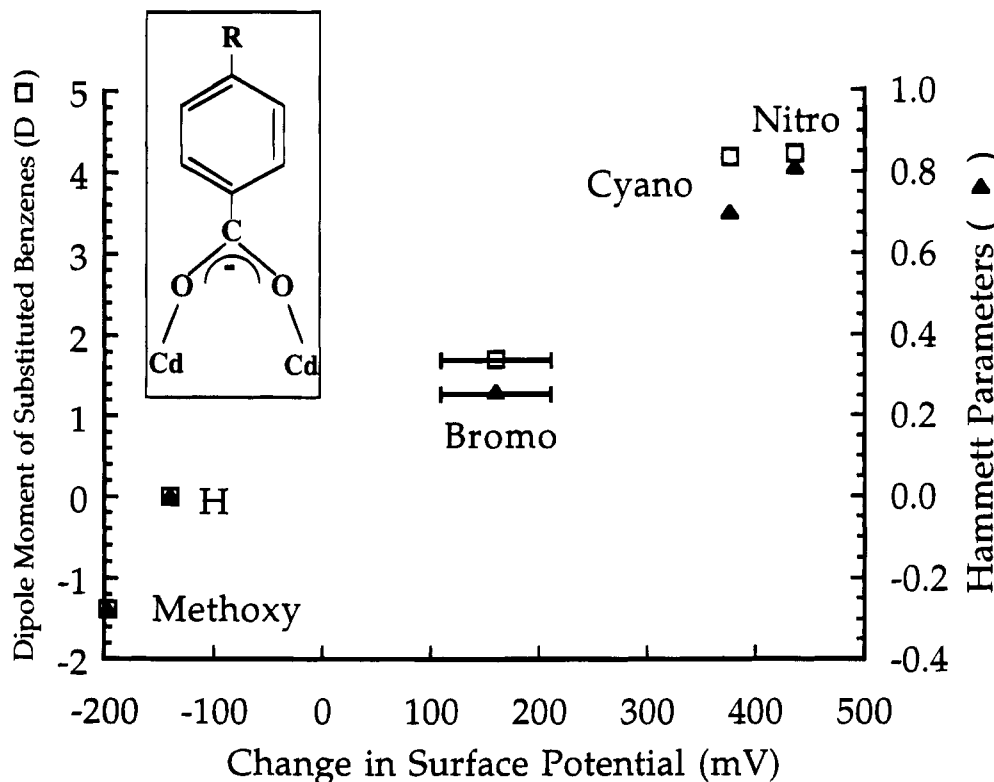


Figure 5. Surface potential of an n-CdSe, single crystal as a function of the Hammett parameters of the adsorbed benzoic acids' substituents³⁰ and of the dipole moments of the corresponding substituted benzenes.³⁷ For clarity, the error bar, which represents the highest observed standard deviation of 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 Cd at the CdSe surface.

TABLE 3: Surface Potential Differences between *p*-Nitro- and *p*-Methoxybenzoic Acid Treated Crystals Using Different Pretreatments and Crystal Faces

pretreatment	crystal face (0001)	surface potential difference between <i>p</i> -methoxy- and <i>p</i> -nitrobenzoic acid treatments (mV)
hydrazine etch ^a	Cd	640 ± 40
hydrazine etch ^a	Se	470 ± 50
Br ₂ /methanol etch ^b	Cd	400 ± 50
Br ₂ /methanol etch ^b	Se	400 ± 90

^a A 100% hydrazine hydrate etch followed a 1% Br₂/methanol etch. See Experimental Section for details. ^b Etched for 2 min in 1% Br₂/methanol.

changes in collection volume (dead layer width) or in (near) surface recombination. These factors can be separated by performing, in addition, transient photoluminescence measurements.^{3,4} The results of those⁸ strongly suggested that the luminescence intensity variations are due to changes in band bending. Therefore, we decided to use the same aniline derivatives to try to induce changes in band bending on n-CdSe and measure this effect by photosaturation experiments. These direct measurements showed that neither *p*-methoxy- nor *p*-cyanoaniline adsorption led to changes in band bending greater than ±50 mV. The difference in the work function changes induced by the two aniline derivatives is 150–200 mV. The experimental conditions necessary to approach surface saturation of the aniline derivatives (0.02–0.04 M solutions in toluene, in accordance with what was used for photoluminescence measurements⁸) may leave some excess aniline derivative on the crystal surface after drying. This might affect the measured surface potential via oriented crystallization but is unlikely to change band bending. In the case of benzoic acid adsorption, excess ligand was not responsible for surface potential changes.

Comparison of Photoluminescence and Kelvin Probe Meth-

ods. The main difference between the Kelvin probe and photoluminescence measurements with aniline derivatives is that the latter were done in solution and the former were done in air. For samples in air, band bending is governed by the population of surface states because no other electronic charge reservoir exists for equilibration with the semiconductor.¹ In solution, work function changes created by dipole adsorption may induce band bending changes by altering the amount of charge transferred between the crystal and the solution upon equilibration of their Fermi levels. We note that other researchers have suggested that GaAs photoluminescence in air is different from that in solution.³² Still not all changes in depletion layer width suggested by photoluminescence can be ascribed to solution effects because some photoluminescence intensity changes have been reported with ligands adsorbed from the gas phase,⁷ i.e., without the possibility of equilibration with a solvent. In recent photoluminescence measurements on benzoic acid treated CdSe,³³ the luminescence intensity gradually decayed to zero upon immersion of the crystal in a benzoic acid solution. Luminescence intensity was also unstable in air. Thus, photoluminescence on benzoic acid treated samples was unable to yield further insight into Kelvin probe–photoluminescence comparisons.

One other possibility for the lack of band bending changes as seen by Kelvin probe methods is that the changes are below our detection limit (≈50 mV). The depletion layer width, *W*, can be related to the band bending, *V_b*, according to

$$W = \left[\frac{2\epsilon\epsilon_0 V_b}{qn} \right]^{1/2} \quad (2)$$

where ϵ is the semiconductor dielectric constant, ϵ_0 is the permittivity of free space, q is the electronic charge, and n is the concentration of free carriers in the bulk. Using a carrier

density of $3 \times 10^{15} \text{ cm}^{-3}$ (typical for the resistivities used by us and in refs 3–8), a dielectric constant of 10,³⁴ and an initial band bending of 450 mV (as we observed), the initial depletion layer width is 400 nm. Changes of 75 nm in depletion layer width, as were reported⁸ (between methoxy- and cyanoaniline treatments) should yield band bending voltage changes of about 150 mV, which can be detected easily by the Kelvin probe. Indeed, changes in band bending between polished and etched crystals are clearly visible (see Table 1).³⁵

Summary of Band Bending Discussion. The most likely reason for the differences in results between the Kelvin probe measurements and the photoluminescence intensity changes is that the latter are due to solution factors. Comparing Kelvin probe and time-resolved photoluminescence measurements on gas phase ligand adsorption should shed more light on these matters.

Conclusions

The surface potential of CdSe crystals can be controlled by etching (to change the band bending and electron affinity) and by adsorbing benzoic acid derivatives (to change the electron affinity). The change in electron affinity scales linearly with the dipole moment of the adsorbed benzoic acid. Adsorption of either benzoic acid or aniline derivatives does not affect the band bending of CdSe in air as measured using the photosaturation technique. Different conclusions from luminescence intensity measurements and Kelvin probe measurements are probably due to the fact that the photoluminescence measurements were done in solution. Thus, contrary to the Kelvin probe measurements which were performed in air, luminescence results probably also reflect interactions with the surrounding medium.

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