

# Controlling the Work Function of GaAs by Chemisorption of Benzoic Acid Derivatives

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Received: August 30, 1996; In Final Form: January 8, 1997<sup>⊗</sup>

Control of the work function of GaAs single crystals, under ambient conditions, was achieved by chemisorption of a series of benzoic acid derivatives with varying dipole moments. Quantitative Fourier transform infrared spectroscopy shows that the benzoic acid derivatives bind as carboxylates, via coordination to oxidized Ga or As atoms, with a surface coverage of about one layer and a binding constant of  $2.1 \times 10^4 \text{ M}^{-1}$  for benzoic acid. Contact potential difference measurements reveal that molecules affect the work function by changing the electron affinity while band bending is not affected significantly. The direction of the electron affinity changes depends on the direction of the dipole moments, and the extent of the change increases linearly with the dipole's magnitude. Investigation of the surface composition by X-ray photoelectron spectroscopy shows that the etched surface, onto which the molecules adsorb, is covered by an oxide layer. This may prevent the molecules from affecting band bending.

## Introduction

Control over the electronic properties of surfaces of semiconductors is of decisive importance for their use in electronic devices. As such it is also critical for electrochemical studies of semiconductors,<sup>1</sup> and for their use in energy conversion and storage applications.<sup>2</sup> The reason is that electron transport across an interface depends on the relative energies of the electronic charge carriers at the free surfaces before their equilibration upon electrical contact. These energies are determined by the structure and composition of the bulk and the surface of the semiconductor.<sup>3</sup> Knowledge<sup>4</sup> and control of them can thus be used for the design of interfaces.

Our approach to interface design utilizes the versatility of molecular (mainly organic) chemistry to modify the surface energetics of semiconductors. The use of molecules to influence electron transfer across semiconductor surfaces is well-known in the area of dye sensitization.<sup>5</sup> There the goal is electron or hole transfer from the molecular electronic excited state to the semiconductor. The approach that is followed here does not require actual electron transfer between the molecule and the semiconductor. Rather, it relies primarily on the effect that the molecules have on the surface energy levels.

Our previous studies have shown that the work function and the electron affinity of several semiconductors (CdTe, CdSe, CuInSe<sub>2</sub>) may be changed by adsorbing a layer of molecules that possess functional groups to bind to the surface as well as auxiliary groups that control the dipole moment of the molecules.<sup>6–8</sup> Here we examine the possible application of the same methodology for the surface modification of GaAs. The extension of this work to GaAs is of importance because of the variety of well-controlled device structures that can be made with GaAs and related materials. Combining that aspect with molecular control can then lead to molecule-based devices.

In contrast to Si, the surface of GaAs is unstable in O<sub>2</sub> and H<sub>2</sub>O-containing atmosphere (i.e., in ambient atmosphere).<sup>9</sup> Thus numerous studies have been carried out to control the surface properties of GaAs.<sup>10,11</sup> Since the first reports of the passivation of GaAs surfaces by inorganic Na<sub>2</sub>S·H<sub>2</sub>O treatments, with

respect to nonradiative recombination,<sup>12</sup> several reports have appeared concerning adsorption of molecules possessing a thiol binding group.<sup>11</sup> It was also reported that organic thiols with various organic functional groups yield substantial reduction in nonradiative surface recombination at GaAs interfaces.<sup>13</sup> In a different way, the ability of thiols to adsorb on GaAs as self-assembled monolayers has been used as electron beam resist.<sup>14</sup>

The study of the effect of the adsorption of benzoic acid derivatives on the electronic properties of GaAs in ambient atmosphere was chosen as a first step toward molecular control of GaAs properties, because binding of benzoic acid derivatives may readily be followed by Fourier transform infrared (FTIR), spectroscopy as the carbonyl frequencies are intense and shift upon surface binding. Moreover, we already have data on surface modifications of other semiconductors with these molecules, thus enabling valuable comparisons to be performed. Finally, examination of benzoic acids that vary in the nature of their substituent at the para position allows systematic modifications of the molecule's dipole moment and quantification of these effects on the surface properties.

## Experimental Section

**Materials.** Polished single crystals of (100) oriented n<sup>+</sup>-GaAs were purchased from American Xtal Technology. Their resistivity was  $1.6\text{--}3 \times 10^{-3} \Omega \cdot \text{cm}$  with  $N_d = (0.7\text{--}1) \times 10^{18} \text{ cm}^{-3}$ . GaAs plates for attenuated total reflectance (ATR) FTIR spectroscopy were purchased from Harrick Co.

Benzoic acid derivatives were commercially available and used as received. The solutions for adsorption were prepared in acetonitrile (HPLC grade). Cleaning and rinsing solvents were analytical grade or better.

Gallium benzoate ( $\text{Ga}(\text{C}_6\text{H}_5\text{CO}_2^-)_3$ ) was synthesized by heating a mixture of gallium (0.17 g) and benzoic acid (10 g) at 220 °C for 36 h. The mixture was then cooled, washed with dry ether, and dried.<sup>15</sup>

**Crystal Treatments.** Cleaning of the samples was done consecutively in boiling trichloroethylene, acetone, and methanol (MeOH), 5 min each. Before adsorption, the surface was prepared by three repeated exposures of the samples to 0.05% (v/v) Br<sub>2</sub>/MeOH and 1 M KOH<sub>aq</sub> for 15 s each (finishing with KOH), then rinsed in water ("bromine etch").

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<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, March 1, 1997.

The ATR crystal was not etched, so as to preserve its optical properties. Between experiments, the ATR crystal was dipped in boiling acetonitrile to remove adsorbed molecules. The efficacy of this treatment was checked by FTIR measurements.

**XPS Measurements.** X-ray photoelectron spectra (XPS) were obtained using Al K $\alpha$  X-ray source and Mg K $\alpha$  X-ray source on a Kratos Axis-HS instrument. The monochromatic Al K $\alpha$  X-ray source (1486.6 eV) was used to obtain chemical information on the As 3d and 2p regions. Measurements were performed with an electron take-off angle of 90°. Samples were introduced in the spectrometer within 15 min after etching.

To get a rough estimate of the overlayer thickness we analyzed the overlayer/substrate intensities in XPS spectra, using the exponential attenuation of the substrate signal.<sup>16,17</sup>

$$I_{\text{sub}}(d_{\text{ol}})/I_{\text{sub}}(0) = \exp(-d_{\text{ol}}/\lambda_{\text{ol}} \sin \theta) \quad (1)$$

where  $d_{\text{ol}}$  is the overlayer thickness,  $\lambda_{\text{ol}}$  the corresponding electron mean free path,  $\theta$  the electron take-off angle, relative to the plane of the surface,  $I_{\text{sub}}(d_{\text{ol}})$  the substrate intensity in presence of the overlayer, and  $I_{\text{sub}}(0)$  the substrate intensity when no overlayer is present. This analysis assumes that all of the material screens electrons equally, depending only on the overlayer thickness. According to ref 18 the electron mean free path in solids has a universal dependence on energy which, for inorganic compounds, is given by

$$\lambda = 0.096E^{1/2} \quad (\text{for } E > 150 \text{ eV}) \quad (2)$$

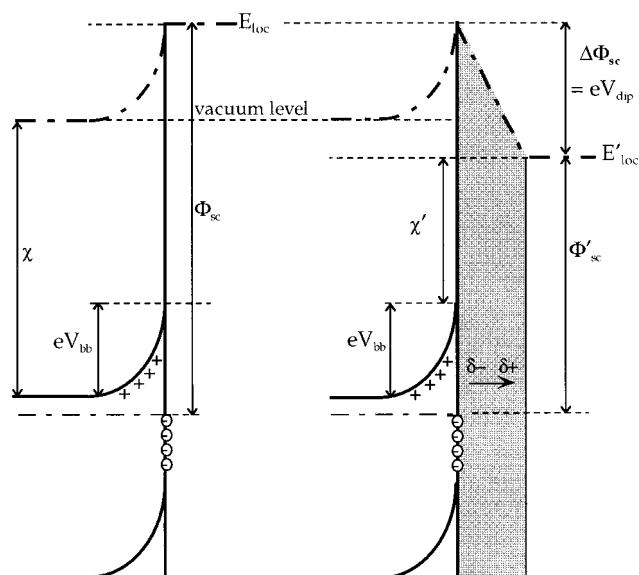
This leads to values of 18 and 12 Å for Ga and As at the 2p level and 37 and 36 Å at the 3d level. Thickness values calculated from eq 1 are meaningful in terms of comparison between samples. In absolute terms, the values become smaller if lower electron mean free paths are assumed. We used a sample sputtered by Ar<sup>+</sup> as a standard sample ( $I_{\text{sub}}(0)$ ). We first sputtered at low voltage (500 V) to remove carbon contamination and most of the Ga and As oxides. However, sputtering at high voltage (4 kV) was necessary to completely remove the oxides.

**Ligand Adsorption.** To adsorb benzoic acid derivatives on GaAs for FTIR studies and contact potential difference (CPD) measurements, we immersed the etched crystal in a 5 mM solution of ligand in acetonitrile for 12 h and subsequently dried the samples by blowing dry N<sub>2</sub> over it.

**FTIR Measurements.** FTIR spectra (Bruker IFS66) of benzoic acid derivatives, adsorbed on single crystals, were measured in different modes. We used mainly the ATR technique, with a parallelepiped-shaped GaAs substrate to achieve good signal–noise ratios. With this sample, the adsorption isotherm of benzoic acid was deduced from FTIR absorption data. The surface benzoate absorption at 1595 cm<sup>−1</sup> was assumed to be proportional to the amount of benzoate on the surface and was converted into surface coverage (number of layers) using a calibration with sodium benzoate as described in the Results and Discussion section. Recording the absorbance at several benzoic acid concentrations provided the data for the adsorption isotherm.<sup>6</sup>

FTIR spectra of benzoic acid and gallium benzoate were measured using KBr pellets made of 150 mg of KBr and 4 mg of these compounds or in Nujol mull.

**CPD Measurements.** We measured the contact potential difference in air using a Kelvin probe apparatus (Besocke Delta-Phi, Jülich, Germany).<sup>19</sup> This method is described in ref 20 and 21. Here we will summarize its principle. The Kelvin probe consists of a closely spaced parallel-plate capacitor made of the semiconductor surface and a vibrating gold gauze



**Figure 1.** Schematic band diagrams of n-type semiconductor surface before (left) and after (right) adsorption of a layer of molecules with a dipole moment pointing away from the surface.  $E_{\text{loc}}$  is the local vacuum level and  $V_{\text{dip}}$  is the potential drop induced by the molecules. The position of  $E_{\text{loc}}$  with respect to  $E_{\text{vac}}$  is given by the potential energy other than that due to the crystal potential.<sup>39</sup> In this figure, the molecules do not affect the band bending.

electrode, whose work function ( $\Phi_{\text{m}}$ ) is assumed to be constant. In equilibrium (electrical connection), the CPD is equal to the difference in their work functions ( $\Phi_{\text{sc}} - \Phi_{\text{m}}$ ). The vibration of the Au electrode leads to a time-dependent variation in capacitance. For a fixed voltage difference due to ( $\Phi_{\text{sc}} - \Phi_{\text{m}}$ ) this forces an ac current to flow through the circuit. The CPD value is measured by means of a variable dc voltage source inserted into the circuit, which is adjusted to zero the ac current.

By measuring the CPD before (B) and after (A) modification of the semiconductor surface (etching, adsorption) we can calculate the change in work function ( $\Delta\Phi_{\text{sc}}$ ), from

$$\text{CPD}^{\text{A}} - \text{CPD}^{\text{B}} = (\Phi_{\text{sc}}^{\text{A}} - \Phi_{\text{m}}) - (\Phi_{\text{sc}}^{\text{B}} - \Phi_{\text{m}}) = \Delta\Phi_{\text{sc}} \quad (3)$$

As shown in Figure 1, the change in work function can be due to a change in electron affinity ( $\Delta\chi$ ), a change in band bending ( $\Delta V_{\text{bb}}$ ), or a combination of both. To distinguish between them, the photosaturation technique was used to measure the band bending.<sup>7</sup> Upon illumination, the photogenerated electron–hole pairs can migrate under the influence of the electric field that exists in the space charge layer, to decrease the space charge and thus the band bending, until the bands become almost flat. A photosaturation curve is given in the Supporting Information which shows that the remaining band bending is less than 40 mV in our experimental conditions (see the paragraph at the end of the paper regarding the availability of Supporting Information). Therefore, the difference between CPD values in the dark and under strong illumination (photosaturation) gives an estimate of the band bending. The illumination source was a 300 W tungsten–halogen lamp, and the intensity was controlled using a variable voltage source.

We measured the CPD (in the dark and under illumination) before and after ligand adsorption. The values reported herein are the average of three sets of experiments, for which six different benzoic acid derivatives have been adsorbed on GaAs samples. Between these three sets, the maximum deviation in measurements after adsorption was 110 mV. Four additional

**TABLE 1: XPS Analysis of GaAs Surface Exposed to Several Etching Procedures<sup>a,b</sup>**

treat- ment	Ga <sub>ox</sub> /Ga <sub>GaAs</sub>		As <sub>ox</sub> /As <sub>GaAs</sub>		As <sup>0</sup> /As <sub>GaAs</sub>		As <sub>As<sub>2</sub>S<sub>3</sub></sub> /As <sub>GaAs</sub>		Ga/As 3d
	2p	3d	2p	3d	2p	3d	2p	3d	
a	0.62	0.20	1.06	0.11					1.2
b	0.37	0.06	0.40 <sup>c</sup>	0.23 <sup>c</sup>	5.00	1.00			0.7
c	0.43	0.09	1.00	0.19					1.2
d	0.29	0.16	0.97	0.11					1.1
e	0.27	0.06	0.36 <sup>c</sup>	0.06 <sup>c</sup>	0.80	0.20	0.32	0.05	1.1
f									1.3

<sup>a</sup> Treatments are given in under Results and Discussion. <sup>b</sup> The subscripts GaAs and Ox refer to bulk and oxidized elements, respectively. As<sup>0</sup> is elemental arsenic. <sup>c</sup> As<sub>GaAs</sub> includes elemental As.

**TABLE 2: Overlayer Thickness after Several Etches,<sup>a</sup> As Derived from XPS Data**

treatment	$d_{ol}^b$ (Å) ± 3 Å from Ga 2p level	$d_{ol}^b$ (Å) ± 2 Å from As 2p level
a	19	19
b	35	27
c	34	30
d	13	13
e	19	17

<sup>a</sup> Treatments are given under Results and Discussion. (d) is the "bromine" treatment used before ligand adsorption. <sup>b</sup>  $d_{ol}$  = overlayer thickness.

sets of experiments were performed, each under experimental conditions slightly different from those used in the experiments reported here. Still, all sets gave qualitatively the same results.

## Results and Discussion

**Characteristics and Suitability of Etched GaAs Surfaces for Adsorption of Molecules.** Different etching treatments were examined by XPS and CPD measurements to find a surface suitable for adsorption of molecules, in terms of reproducibility of the results and defined surface composition. The treatments are the following:

(a) unetched sample cleaned in trichloroethylene, acetone, MeOH

(b) H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O (8:1:100 v/v) for 1 min

(c) same as (b), followed by three treatments with 0.05% (v/v) Br<sub>2</sub>-MeOH (15 s) and then 1 M KOH (15 s)

(d) three times 0.05% (v/v) Br<sub>2</sub>-MeOH (15 s) and then 1 M KOH (15 s), "bromine etch"

(e) H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>O (1:8:500 v/v) for 1 min, then immersion in 1 M Na<sub>2</sub>S for 2 h and rinsing with deionized water

(f) Ar<sup>+</sup> sputtering

**XPS Measurements.** After etching, the samples were dried with N<sub>2</sub> gas and placed into the XPS chamber. As a result, the samples were exposed to air for 10–15 min. XPS data are reported in Table 1. The overlayer thickness, as calculated from the intensities of the As 2p and Ga 2p signals, with respect to those of the sputtered sample (f), are given in Table 2. The error range is calculated from the overall reproducibility of the XPS sensitivity. Note that the sputtered sample is Ga rich (Ga/As<sub>bulk</sub> = 1.3), which may lead to some additional errors in the calculated thicknesses since treated samples have different stoichiometry. However, for treated samples with Ga/As<sub>bulk</sub> in the range 1.1–1.2, a good agreement is found between values obtained using either As or Ga 2p signals, indicating that differences in stoichiometry induce errors that are negligible compared to other sources of errors. The only exception is treatment (b) for which the strong difference in bulk stoichiometries ((b) 0.7; (f) 1.3) may be responsible for the discrepancy in thicknesses. This can also be due to an uncertainty in the

deconvolution of the As<sup>0</sup> and As<sub>sub</sub> signals, since the peak of the former is much larger and overshadows that of As<sub>sub</sub>.

Oxygen, bound to Ga and As, is found, after all types of etching treatments. This is more pronounced from the 2p than from the 3d data, indicating that the atoms in the upper layer are more oxidized (the difference in kinetic energy between the 2p and 3d photoelectrons is such that the escape depth of electrons from the former is smaller than that of the latter, by factors of 2 for Ga and 3 for As). The chemical shifts measured for the Ga and As levels after acid etching (b) are, respectively, 1.1 and 3.4 eV for the 2p levels and 1.3 and 3.2 eV for the 3d levels. After bromine etching (d) the shifts are 0.9 and 3.0 eV for the 2p level and 1.1 and 3.0 eV for the 3d level, which is in good agreement with those reported earlier<sup>10,22</sup> and indicate the presence of the oxidized species Ga<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>O<sub>3</sub>.

The oxide formation may occur during etching, during exposure to air before XPS measurements, or during both. For acid etches, Massies and Contour have shown that the presence of oxide was due to exposure to air and not to the etching itself.<sup>22</sup> They calculated an increase in the oxide ratio ( $I_{ox}/(I_{ox} + I_{sub})$ , As 2p level) from 0 to 0.5 after 15 min exposure to air while in our case this ratio is 0.7 after the same period of time. In the case of the bromine etch, this ratio is 0.5. Moreover, with the same etching conditions, Lunt et al. found no oxide when exposure to air was excluded.<sup>13</sup> This indicates that oxide formation may be mainly due to the exposure of samples to air atmosphere, rather than to the wet etching treatment.

It has been reported that GaAs surfaces are covered by a 30 Å thick native oxide layer after about 4 days in air.<sup>23</sup> The relatively small thickness observed on our unetched samples (19 Å) may be due to the effect of solvents during the cleaning procedure, particularly MeOH, which acts as a complexant of oxides in bromine etch.

As expected, acid etch (b) leads to an enrichment in As (As<sup>0</sup>) of the surface (chemical shift of 0.7 eV/As<sub>GaAs</sub><sup>13</sup>). Consistent with the work of Stocker and Aspnes,<sup>24</sup> we observed that the As<sup>0</sup> film is readily removed by the bromine etch. After etch (b) the ratio Ga/As is 0.7, whereas after the bromine etch (c) it becomes 1.2. Etch (b) leads to a high overlayer thickness, since elemental As is precipitated on the surface while the bromine etch is found to produce a smaller overlayer (oxide) thickness (d). However, when the bromine etch followed the acid etch (c), we found a thicker oxide overlayer compared to (d).

The results also indicate an overlayer coverage of As<sub>x</sub>S<sub>y</sub> after exposure of GaAs to Na<sub>2</sub>S solution (1 M). From literature data, it is also clear that the Na<sub>2</sub>S treatment removes excess As<sup>0</sup>, as can be seen from the change in Ga/As ratio between (e) and (b) (As includes As<sub>GaAs</sub> and As<sup>0</sup>).<sup>13</sup> The presence of an As-S phase was apparent from peaks at 43.3 and 1325.1 eV for the As 3d and 2p regions, respectively. With the same treatment, Lunt et al. obtained similar values and attributed these binding energies to an As<sub>x</sub>S<sub>y</sub> phase.<sup>13</sup>

Since the bromine etched surfaces show the least oxide, no detectable amount of As<sup>0</sup>, and a stoichiometric ratio, this etch seemed to be the more suitable one for the adsorption of benzoic acid derivatives on GaAs. Still, we stress that adsorption occurs on an oxidized surface.

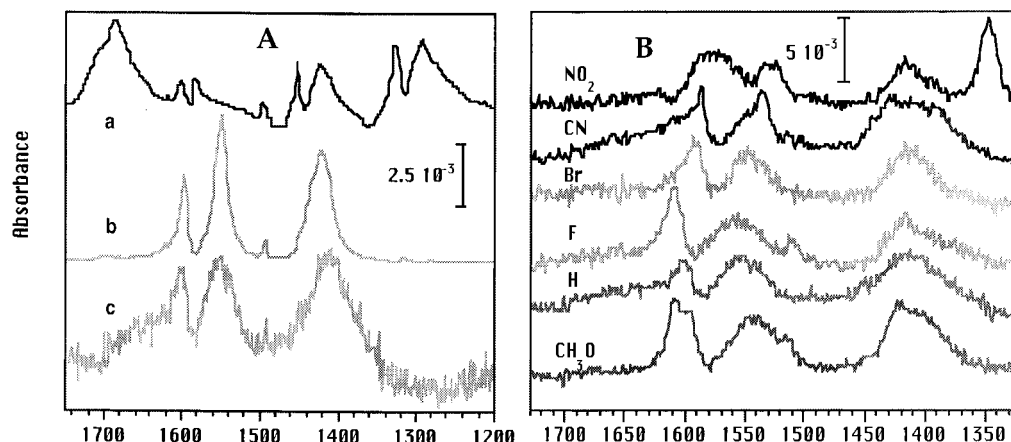
**CPD Measurements.** Table 3 gives the changes in  $\Phi_{sc}$  and  $V_{bb}$ , measured after acid and bromine etches, (b) and (d) respectively, with respect to unetched samples (a). Moreover, an additional H<sub>2</sub>O<sub>2</sub> treatment (30% for 2 min at ambient temperature) was performed after etch (d) to analyze the effect of oxidation.

Compared to unetched samples, acid etch (b) leads to an increase in the work function (from 4.60 to 5.10 eV) and no

**TABLE 3: Changes in Work Function and Band Bending of GaAs after Several Etching Procedures<sup>a,b</sup>**

treatment	surface composition	$\Delta(\text{work function})$ (mV)	$\Delta(\text{band bending})$ (mV)
a	oxide layer, excess Ga	0 (4.60 V)	0 (400 mV)
b	thick overlayer, oxide, excess As <sup>0</sup>	+500	0
d	thin oxide layer, stoichiometric	+300	+300
d + H <sub>2</sub> O <sub>2</sub> <sup>c</sup>	oxide layer	0	-50

<sup>a</sup> Treatments are given under Results and Discussion. <sup>b</sup> Unetched sample characteristics are taken as reference (absolute values given in parentheses). <sup>c</sup> 30% H<sub>2</sub>O<sub>2</sub> 2 min at ambient temperature.



**Figure 2.** (A) FTIR spectra of (a) benzoic acid in KBr, (b) gallium benzoate in KBr (results in Nujol mull are virtually identical), and (c) a benzoic acid-treated GaAs ATR plate. Spectrum c is on a two times more sensitive scale than indicated. (B) FTIR spectra of benzoic acid derivatives adsorbed on GaAs ATR plate. The para substituent of benzoic acid is indicated. The spectra are displaced along the y-axis for the sake of clarity. For details, see the Experimental Section.

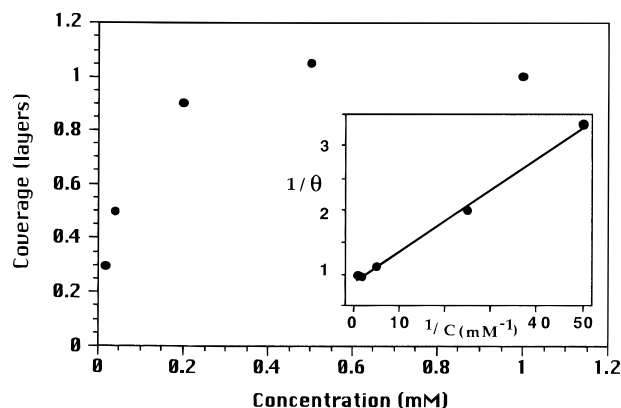
change in band bending, which means that it is mainly due to an increase in the electron affinity. Since the work function of As<sup>0</sup> is 3.75,<sup>25</sup> an increase in work function should not be expected. We assume that it is due to the high porosity reported for the As<sup>0</sup> film (0.78) by Stoker and Aspnes.<sup>24</sup> They attributed the good Schottky behavior of diodes made by deposition of InP on such surfaces to the 0.22 volume fraction of the film, which is far below the percolation threshold for electrical conduction. Therefore the reverse leakage current of their diodes is very small (16  $\mu\text{A cm}^{-2}$  at -10 V for a In<sub>0.53</sub>Ga<sub>0.47</sub>-As/InP mesa photodiode). The reason may be the depletion of electronic carriers in such a composite As<sup>0</sup> layer, as has also been reported in the nanometer-size silicon crystallites of highly porous silicon.<sup>26</sup> The increase in EA of GaAs after acid etch is then consistent with the As<sup>0</sup> film properties reported in ref 24, although in our case the surface is oxidized and other factors can induce this increase, such as a change in surface dipole moment due to the presence of As<sup>0</sup>.

Bromine etch (d) is also found to increase the work function but to a lesser extent than acid treatments. Contrary to the latter, it is the band bending which is modified rather than the electron affinity, when compared to the unetched sample. A change in electron affinity would be expected if the etching treatment removed the oxide layer and, therefore, changed the surface dipole moment. However, after bromine etch and exposure to air, the surface is still slightly oxidized, as observed by XPS. Therefore, the dipole moment effect due to the oxidized species is present before as well as after the etch causing no change in electron affinity. We used H<sub>2</sub>O<sub>2</sub> (Table 3, d + H<sub>2</sub>O<sub>2</sub>) to reoxidize the bromine-etched surface to a larger extent, to confirm these conclusions. When considering the sequence (a), (d), (H<sub>2</sub>O<sub>2</sub>), CPD data show that bromine etch leads to an increase of band bending while, when reoxidized, it decreases to approximately the same value as that of the unetched sample. It can therefore be concluded that the amount of oxide controls the band bending, i.e., the Fermi level position.

**Adsorption of Benzoic Acid Derivatives: Characteristics of the Adsorption Mode and Modification of GaAs Electronic Properties.** *FTIR Analysis.* Figure 2A shows FTIR spectra of (a) benzoic acid in a KBr pellet, (b) gallium benzoate in a KBr pellet, and (c) adsorbed benzoic acid on a GaAs ATR crystal. Upon adsorption on GaAs, the carbonyl frequency (Figure 2A(a), 1687  $\text{cm}^{-1}$ ) is replaced by the carboxylate frequencies (Figure 2A(c), 1550 and 1410  $\text{cm}^{-1}$ ). This is in agreement with the change occurring when benzoic acid is transformed to benzoate, as in the formation of gallium(III) benzoate (Figure 2A(b)). In light of these spectra it can be concluded that benzoate derivatives form a coordination complex on the surface. The most likely coordination sites are oxidized Ga or As on the surface. In analogy to what has been found on oxidized metals, it seems likely that surface O atoms act as basic site to deprotonate the acid group.<sup>27</sup> This process will create a free coordination site on some close (still oxidized) Ga or As atoms for the conjugated benzoate. Considering that Ga is more electropositive than As, it is likely that the adsorbed species are Ga- rather than As-coordinated benzoates.<sup>28</sup>

Figure 2B shows FTIR spectra obtained in six separate experiments with the ATR crystal, onto which any of the six benzoic acid derivatives was adsorbed. The low signal to noise ratio is due to the fact that we are looking at single layer coverage (see below). As already mentioned, the absence of the carbonyl peak of the protonated acid in all cases indicates that the molecules do not precipitate unbound on the surface.

The splitting between the symmetric and asymmetric vibrational modes of the carboxylate ion (around 1550 and 1420  $\text{cm}^{-1}$ , respectively) is an indication of the coordination mode.<sup>29</sup> Compared with the splitting value of the free carboxylate (144  $\text{cm}^{-1}$ ), a unidentate complex exhibits larger splitting values while a bidentate complex shows smaller ones (changes of +70 and -70  $\text{cm}^{-1}$ , respectively, in the case of acetate complexes). In the case of the bridging coordination mode, however, small changes are observed ( $\pm 25 \text{ cm}^{-1}$  in the case mentioned above)



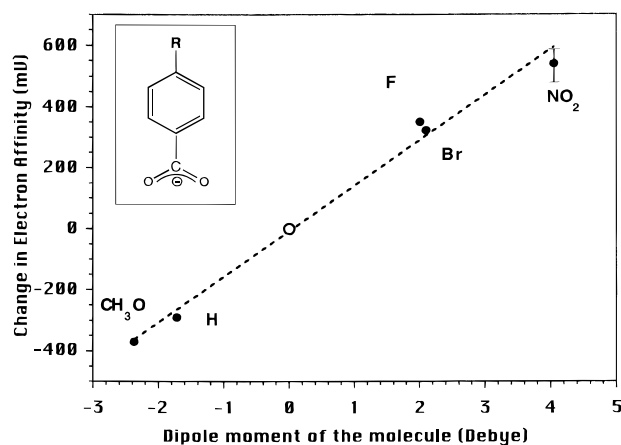
**Figure 3.** Adsorption isotherm of benzoic acid on GaAs ATR plate, obtained from quantitative FTIR spectroscopy, using the surface benzoate absorption at  $1590\text{ cm}^{-1}$ . Plot of the reciprocal of coverage as a function of the reciprocal of concentration according to the Langmuir isotherm model is shown in the insert.

relative to the free carboxylate. Compared to the splitting value of free benzoate (Figure 2A), only a small deviation of those of adsorbed benzoates is observed (Figure 2B:  $-35\text{ cm}^{-1}$  for CN substituent and  $\pm 20\text{ cm}^{-1}$  for the others), which therefore suggests bridging mode complexation, probably to Ga.

**Surface Coverage, Adsorption Isotherms.** We used FTIR absorption data to assess surface coverage. We first calculated the amount of benzoic acid in a single layer, assuming a flat surface and a surface area of  $25\text{ Å}^2$  per molecule.<sup>6</sup> This is a reasonable estimate for the surface area occupied by a molecule containing a benzene ring, but the area may increase somewhat if the molecule is highly tilted from the surface normal. We then spread a solution containing this amount of sodium benzoate on the substrate. The solvent evaporated, and the subsequent FTIR absorbance at  $1595\text{ cm}^{-1}$  was measured as a point of reference. By using solutions of lower concentration and by taking the values obtained then as the absorbance of fractions of a layer, we obtained a calibration curve which was linear. Using this calibration, the amount of benzoic acid that is adsorbed on the surface was estimated.

Figure 3 shows the adsorption isotherm of benzoic acid on a GaAs ATR substrate. The isotherm suggests that a  $0.5\text{ mM}$  concentration of benzoic acid is sufficient to saturate the surface of the ATR substrate with one layer. We note, though, that this experiment cannot be performed at ligand concentrations  $> 10\text{ mM}$ . At high ligand concentrations, excess unbound ligand collects on the surface and obscures binding peaks. The insert of Figure 3 shows the plot of the reciprocal of coverage as a function of the reciprocal of concentration. According to the Langmuir isotherm model, this plot should be a straight line, intercepting the y-axis ( $C = 0$ ) at 1. It can be seen that the adsorption data are in good agreement with the model. The binding constant  $K$  deduced from this plot is equal to  $2.1 \times 10^4\text{ M}^{-1}$ . For benzoic acid adsorbed on CdTe and ZnSe ATR plates, we found  $K$  equal to  $1.3 \times 10^3$  and  $6.3 \times 10^3\text{ M}^{-1}$ , respectively.<sup>30</sup> Therefore, binding of benzoic acid seems to be stronger on ambient-exposed ATR plates of GaAs than on those of CdTe and ZnSe. These data agree with literature values for binding of Ga and Cd to carboxylic (citric) acids.<sup>28</sup>

**Electron Affinity Changes upon Adsorption.** Figure 4 shows the relationship between the adsorbed ligand's dipole moment and the change in electron affinity of a GaAs (100) surface. The dipole moments are taken from measurements made in dioxane solvent.<sup>31</sup> In our previous reports on benzoic acid adsorption onto semiconductors the dipole moment of the substituted benzene was used. Here the dipole moment of the



**Figure 4.** Change in electron affinity of GaAs, after adsorption of benzoic acid derivatives, as a function of the dipole moment of the derivative (R, insert). The para substituent of the benzoic acid is indicated in the figure. The error bar (deviation of three measurements) is shown for the  $\text{NO}_2$  derivative. The open circle represents the theoretical zero point (0 D, 0 mV).

benzoic acid derivative is used instead; i.e., the effect of the carboxylic acid group is included. Similar to what we reported before, for CdTe, CuInSe<sub>2</sub>, and CdSe,<sup>6-8</sup> the electron affinity of GaAs varies linearly with the ligand's dipole moment. Furthermore, the case of a zero dipole moment (no induced change in electron affinity) fits well with the data reported here (open circle in Figure 4).

These data may be understood as follows. The change in electron affinity due to the molecule's dipole moment can be described in terms of a parallel plate capacitor. Elementary electrostatics leads to the well-known Helmholtz equation, where the potential drop  $\Delta V$ , due to the dipole layer, is given by

$$\Delta V = N\mu(\cos \theta)/\epsilon\epsilon_0 \quad (4)$$

Here  $\mu$  is the dipole moment,  $N$  the dipole density per unit area,  $\theta$  the angle between the dipole and the surface normal,  $\epsilon$  the relative permittivity of the film, and  $\epsilon_0$  the permittivity of free space.<sup>32</sup> When values for  $N$ ,  $\cos \theta$ , and  $\epsilon$  are known,  $\Delta V$  can be calculated.

The linear dependency of  $\Delta V$  ( $V_{\text{dip}}$  in Figure 1) on  $\mu$  implies that  $N$ ,  $\cos \theta$ , and  $\epsilon$  are constant for the benzoate derivatives used here.  $N$  and  $\cos \theta$  depend on geometrical factors, namely on the molecule's footprint area and on the molecule's length. Since these parameters are almost identical between the derivatives,  $N$  and  $\cos \theta$  are indeed likely to be constant.

$\epsilon$  cannot be taken as an ordinary dielectric constant since it is related not to a macroscopic system (bulk material) but to a special microscopic system (one layer of packed molecules, not necessarily well-organized). It is introduced here to take into account the polarizability  $\alpha$  of the molecules, which causes a depolarizing field at the position of a given dipole, arising from all surrounding dipoles.  $\alpha$  is usually on the order of the molecular volume and then does not differ very much between the benzoic acid derivatives.

Several authors have given self-consistent microscopic treatments of planar interactions in monolayers, which leads to expressions of  $\epsilon$  as a function of the dipolar properties and surroundings of molecules in such films.<sup>33,34</sup> However, these formulas are found to give much higher  $\Delta V$  values (few volts) than observed experimentally.

A better approach for our purpose may be one based on experimental results obtained with Langmuir films. Several studies have been carried out on Langmuir films assembled at

water/air interfaces to relate CPD measurements of the voltage drop occurring in the film to the dipole moment of the molecules. The dipole moment can be estimated accurately from  $\Delta V$  by comparing experiments in which the head group (in contact with water) or the tail (in the air) of the molecules are changed. Dipole moments obtained in this manner are in very good agreement with values measured with other methods. The relative permittivities of monolayers of different kinds of molecules were deduced from such measurements.<sup>35,36</sup> The values that are obtained for aromatic molecules and carboxylic acid head groups roughly lie between 5 and 8. Using these and assuming that the surface is covered by one layer of ligand with a density of 1 dipole/25 Å<sup>2</sup>,  $\Delta V$  could be 1.9–1.2 V (for  $\epsilon = 5$  and 8, respectively) when the dipole moment is changed by 6.4 D, as is the case when replacing methoxy (−2.37 D) by nitro (4.05 D) substituents.

These values are higher than the ones we measured. From eq 4 we see that this discrepancy can be due to the coverage ( $N$ ), the tilt ( $\cos \theta$ ), and/or the permittivity ( $\epsilon$ ). The tilt affects the magnitude of the dipole moment (perpendicular component to the surface) together with the dipole density (since tilting the molecule increases the area it occupies by a factor of  $1/(\cos \theta)$ ). Therefore, a tilt by 30°–45° may explain the difference between the measured (0.9 V) and the calculated values (1.2–1.9 V, respectively).

Another discrepancy is the order of the fluoro and bromo derivatives which does not fit the general trend. This was also seen for CdTe.<sup>6</sup> The fluoro derivative has a slightly smaller dipole moment than the bromo (2.0 and 2.1, respectively) but gives a larger change in electron affinity. We noted already that  $\epsilon$  depends on the polarizability  $\alpha$ . The highest  $\alpha$  is estimated to be  $17.7 \times 10^{-24} \text{ cm}^3$  (nitro or bromo substituted) while the lowest is  $13.0 \times 10^{-24} \text{ cm}^3$  (benzoic acid), leading to a maximum difference in  $\alpha$  by a factor of 1.3.<sup>25</sup> The discrepancy between the fluoro and the bromo derivative is then probably due to the difference in their polarizabilities ( $13.3 \times 10^{-24} \text{ cm}^3$  vs  $17.3 \times 10^{-24} \text{ cm}^3$ ). The lower polarizability of the fluoro derivative results in a lower relative permittivity  $\epsilon$  (i.e., a higher voltage drop in eq 4) compared to the bromo derivative. Their identical dipole moments make this difference more noticeable than for other derivatives.

Comparing the above results to those earlier obtained for CdTe and CdSe,<sup>6,7</sup> we note a much larger change in surface potential (150 mV/D for GaAs, 100 mV/D for CdSe, and 60 mV/D for CdTe) when the data for those compounds are plotted in the same fashion as those for GaAs are in Figure 4. These differences can also be expressed in terms of Hammett's  $\rho$  parameter, obtained from the slope of  $\Delta V$  versus Hammett's  $\sigma$  parameters.<sup>37</sup> Those values (6 for GaAs, 4 for CdSe, and 2.5 for CdTe) are for the reaction of benzoic acid with the semiconductor surface. The discrepancy can be due to differences in coverage or in tilt angle. Tilt differences could explain the results, if the average angle of the molecular dipole were 30° for GaAs and 55° for CdTe. Different coverages could arise from differences in adsorption site density or from the observed differences in binding constants of benzoic acids to GaAs and CdTe.

**Band Bending Changes.** In contrast to the observed change in electron affinity (Figure 4), we could not observe reproducible trends of changes in band bending upon adsorption of benzoic acid derivatives. This was also the case for CdTe, CuInSe<sub>2</sub>, and CdSe.<sup>6–8</sup> The changes were between −150 and +50 mV, which is relatively small compared to the error range of the experiment ( $\pm 50 \text{ mV}$ ).<sup>38</sup>

Lunt et al. have shown that adsorption of sodium methoxide onto GaAs yields substantial increases in the steady-state photoluminescence intensity. They interpreted this as being due to a change in the surface Fermi level position. In their case, the GaAs surface was treated in a manner to prevent oxidation.

From XPS experiments it is clear that in our case an  $\approx 15 \text{ Å}$  thick oxide layer exists on the GaAs surface after bromine etch. The presence of this layer can explain the observed electronic behavior of GaAs upon adsorption of benzoic acid derivatives. Thus, even though oxide species dictate the Fermi level pinning at the surface (and thus the band bending), as shown by CPD data for etched surfaces, they do not prevent the molecules changing the semiconductor's electron affinity.

## Conclusion

FTIR spectra of benzoic acid derivatives adsorbed on air-exposed GaAs single crystals show that the carboxylate group binds to Ga in the bridging coordination mode, probably to Ga. Langmuir isotherms show that around one layer of molecules is present after adsorption. Comparison of the binding constant value deduced from the isotherm with that for binding to CdTe shows stronger binding to the oxidized GaAs surface than to the oxidized CdTe one. CPD measurements show that adsorption of these molecules changes the work function of GaAs, and comparison of CPD in light and dark measurements indicates that this change in work function is due to a change in electron affinity. The variation in electron affinity is linearly proportional to the dipole moment of the molecule. The extent of the variation of the electron affinity is much larger than what was found earlier for CdTe and CdSe, reaching nearly 1 V when the dipole moment is varied by 6.4 D (nitro and methoxy substituents). No change in band bending could be observed within experimental error. The less than theoretically expected extent of change in electron affinity can be due to an average tilt of  $\approx 30^\circ$ – $45^\circ$  of the molecules. The larger effect on GaAs than on CdTe and CdSe is ascribed to stronger surface binding. The lack of change in band bending may be due to the presence of oxides on the surface which dictates the Fermi level position and prevents molecules from influencing the band bending.

Adsorption of benzoic acid derivatives allows control of the GaAs electron affinity, independently of the band bending, when no precautions are taken against oxidation. Experiments under controlled atmosphere (free of oxygen and H<sub>2</sub>O) and experiments using dicarboxylic acid derivatives are currently under way. These may provide new insights in the potential of molecular binding for tailoring the electronic energetics of GaAs surfaces.

**Acknowledgment.** This research is supported by a grant of the Israel Ministry of Science and the Arts and of the Research Centre Jülich GmbH (KFA), Project for Biology, Energy and Ecology, and by the Minerva Foundation (Munich). We thank Dr. Hagai Cohen for XPS measurements. A.S. holds the Siegfried and Irma Ulman chair. S.B. acknowledges a Feinberg Graduate School postdoctoral fellowship.

**Supporting Information Available:** Table S.1 listing FTIR frequencies of benzoic acid derivatives adsorbed on GaAs ATR substrate and Figure S.1 showing change of CPD as a function of light intensity (2 pages). Ordering information is given on any current masthead page.

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