

observe the (00 $\bar{l}$ ) reflection of hcp palladium particles by XRD. This supports the assumption that the particles are quasi two-dimensional in shape, since a limited thickness (of at least three unit cells) is necessary to observe (00 $\bar{l}$ ) reflections. According to the theoretical prediction of ferromagnetism in Pd [8] and the experimental evidence of ferromagnetism [9], these particles should comprise a thickness of 2–5 layers, i.e., insufficient to generate (00 $\bar{l}$ ) reflections. Furthermore, not all particles have the same thickness (evidence for which can be seen by the differing absorptions within the electron beam, see TEM images). Nanoparticles were been observed by a Hitachi 9000 transmission electron microscope (TEM) operated at a 300 kV accelerating voltage. The structure was determined by SAED. Raman microscopy showed that no charge transfer interaction between carbon and palladium metal existed [15]; the particles were electronically separated. Therefore, they are not longer a common graphite intercalation compound. A more detailed study of the physical and chemical nature (such as magnetic measurements and catalytic properties [15]) of these particles is now in progress.

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## Frontier Orbital Model of Semiconductor Surface Passivation: Dicarboxylic Acids on n- and p-GaAs\*\*

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Most semiconductor surfaces feature surface states, i.e., defect energy states inside the otherwise forbidden energy gap of the semiconductor. These defect energy levels differ

from those that make up the valence and conduction bands in that the electronic charge in them is *localized*. On n-type semiconductors, we often find that surface states close to the valence band (VB) dominate. These states are usually filled with electrons and are negatively charged. Conversely, on p-type semiconductors, we often find the dominating surface states to be hole-filled, positively charged, and close to the conduction band (CB).<sup>[1–3]</sup>

The interest in studying surface states stems from the decisive effect that they can have on the performance of many, if not most, electronic devices. This is because surface states play a significant role in electronic transport across device interfaces, by a combination of two mechanisms:<sup>[1–3]</sup>

- Surface-state occupation governs the surface charge. The latter affects the band bending, i.e., the electrical potential barrier present at semiconductor surfaces and interfaces.
- Surface states affect trapping and recombination of excess charge carriers.

Inorganic<sup>[1–3]</sup> and organic<sup>[4–8]</sup> chemical treatments, designed to improve the surface and interface electronic quality by “passivating” the surface, have been used for many years. While it is accepted in general terms that such passivation<sup>[9]</sup> modifies the surface states and associated properties, understanding of the molecular and atomic parameters that induce the modifications, as well as the mechanism(s) by which these modifications happen, is still limited.

Chemisorption of molecules on semiconductors can be viewed in terms of molecule-induced surface passivation, and the interaction of a given molecule with a given solid surface can be considered in terms of generalized acid–base behavior (a special, extreme case of which is oxidation–reduction, i.e., the molecule accepts or donates an electron<sup>[10–12]</sup>). However, passivation is a wide, somewhat vague term that does not give any information about molecule-induced changes in the density and energy distribution of surface states. Such effects can be described if we use the frontier orbital description of acid–base reactions.<sup>[11,12]</sup> In this approach we consider the interaction between the highest occupied molecular orbital (HOMO) of the solid or the molecule and the lowest unoccupied molecular orbital (LUMO) of the other.<sup>[13]</sup> The driving force for the interaction is the stabilization of the occupied states and therefore the reduction in the electronic free energy of the new molecule–solid system.

In a qualitative fashion, frontier orbitals were invoked by Nelson et al. to explain effects of chemical treatments on the surface recombination of GaAs<sup>[14]</sup> and by Ellis and co-workers to explain changes in the photoluminescence (PL) intensity of n-CdSe and CdS crystals after interaction with different organic acids and bases.<sup>[5,15]</sup> More recently, similar ideas were used by Liu et al. to explain the selective interaction of Br<sub>2</sub> with the GaAs(001) surface.<sup>[16]</sup> They argued that the HOMO level of the molecule interacts with the unoccupied, LUMO-like state of the Ga dangling bond, whereas the LUMO level of the molecule interacts with the filled, HOMO-like states of the As.

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In previous work, we have shown that the net charge of the n-CdTe(111) surface, which dictates the surface band bending,  $V_s$ , via the Poisson equation, could be tuned by chemisorbing a series of dicarboxylic acids (DCAs).<sup>[17]</sup> By comparing the change in  $V_s$  with the molecule's estimated LUMO energy, we showed that the changes in  $V_s$  are controlled by two contributions. The first contribution was constant for all the DCAs studied and was related to the molecular binding group. The second contribution, which was mostly more significant than the first one, depended on the energy difference between the DCA's LUMO and the surface state levels. The smaller this difference, the stronger the molecule-surface state coupling, and consequently the larger the change in  $V_s$ .

The advantage of considering surface passivation in terms of frontier orbital interactions rather than generalized acid-base ones becomes apparent when comparing molecular effects on surfaces of p- and n-type samples. In the generalized acid-base model, the character of the surface states and their detailed energy position are not considered. That is because the molecule either accepts electronic charge (i.e., is reduced) or donates it (i.e., is oxidized). Thus, the surface of p- and n-type samples should both become either more positive or more negative upon the same molecular treatment.<sup>[18]</sup> In the frontier orbital model, however, the response of a given semiconductor may well depend on the detailed character of the surface states. For example, the model distinguishes between the interaction of a given molecular LUMO state with filled surface states, dominant in n-type semiconductors (LUMO-HOMO interaction), and the interaction with unoccupied states, dominant in p-type semiconductors (LUMO-LUMO interaction).

For a meaningful comparison between the surfaces of p- and n-type samples, all surfaces examined must retain a similar structure and composition, which is independent of the bulk type. Also, the surface state density should not be so large as to fix the Fermi level with respect to the band edges (i.e., the surface Fermi level should not be "pinned" by the surface states<sup>[2,3]</sup>). We have investigated a number of oppositely doped pairs of semiconductor samples, namely, CdTe, InP, and GaAs. While large differences between the electron affinity of p- and n-type CdTe and InP ruled out their use, the GaAs(100) surface presented a reasonable fit to our requirements.

Here we use the effects of adsorbing different DCAs on the surfaces of oppositely doped GaAs samples to study experimentally the molecular effects on surface-state energy levels and to correlate these level changes with surface band bending effects.<sup>[19]</sup> Our results show the predictive power of the frontier orbital model for semiconductor surface passivation.

p-GaAs(100) samples ( $2 \times 10^{17} \text{ cm}^{-3}$ , ITME, Poland) and n-GaAs(100) samples ( $3 \times 10^{18} \text{ cm}^{-3}$ , referred to as type I, and  $5 \times 10^{16} \text{ cm}^{-3}$ , referred to as type II, both from AXT, USA) were used in this study as they exhibited the smallest

difference in their surface potential. In order to compare to and build on earlier results, we used molecules of a series studied earlier with the n-CdTe(111) surface, namely dicyano-, dihydrogen- and dimethoxy-dicarboxylic acids (DCDC, DHDC, and DMDC respectively).<sup>[17]</sup> Prior to molecule adsorption, the samples were etched with  $\text{Br}_2/\text{MeOH}$  (0.05 % v/v) and KOH (1 M) solutions. The samples were dipped overnight in a 2.5 mM molecular solution in acetonitrile (high pressure liquid chromatography or spectroscopic grade). After adsorption, the samples were rinsed with pure acetonitrile to remove excess unbound molecules. Fourier transform infrared (FTIR) spectroscopy was applied to characterize the surface after molecule adsorption and indicated one strongly chemisorbed monolayer (with binding constants of  $3 \times 10^6$  and  $3 \times 10^5 \text{ M}^{-1}$  for DCDC and DHDC on n-GaAs, respectively<sup>[20]</sup>). Previous work has established the presence of oxidized species on the surface, mainly  $\text{Ga}_2\text{O}_3$  and  $\text{As}_2\text{O}_3$ .<sup>[21]</sup> Thus, the molecule is bound via coordination to the oxidized Ga or As atoms.

Molecular effects on the surface-state energy position and surface band bending were determined by surface photovoltage spectroscopy (SPS) and photosaturation, respectively. SPS is based on recording the contact potential difference (CPD, defined as the difference between the work function of the semiconductor and that of a reference electrode), as a function of incident photon energy.<sup>[22,23]</sup> The technique allows the determination of the energy position of surface states, relative to the band edges, as well as the type of electronic excitation involved (from surface states to band edge or from band edge to surface states). This is achieved by observing threshold energies for sharp changes in the CPD signal and the sign of those changes, respectively. Photosaturation is based on subtracting the CPD value under intense illumination, where  $|V_s|$  is ideally nullified, from its value in the dark, where  $|V_s|$  is maximal. This yields a lower limit to the surface band bending.<sup>[24]</sup>

CPD spectra of the n-GaAs (type I) and p-GaAs surfaces, before and after adsorption of DCDC, are shown in Figure 1. The CPD change at  $\sim 1.4 \text{ eV}$  corresponds to the onset of band-to-band absorption in GaAs. Its positive or negative sign indicates p- and n-type samples, respectively. The decrease of the CPD change at the bandgap energy upon DCDC adsorption indicates a molecule-induced reduction of  $|V_s|$ . The bare surface of the p-GaAs samples features a positive CPD change at  $\sim 0.9 \text{ eV}$ . This indicates electron transitions from the VB maximum into surface states situated  $\sim 0.9 \text{ eV}$  above it, i.e., closer to the CB minimum. The bare surface of the (type I) n-GaAs samples features a negative CPD change at  $\sim 1.2 \text{ eV}$ . This indicates electron transitions to the CB from surface states situated  $\sim 1.2 \text{ eV}$  below the CB minimum, i.e., closer to the VB maximum. Upon DCDC adsorption, the sub-bandgap transition in both p- and n-type samples decreases strongly, indicating a reduction of the surface state density inside the bandgap. Photosaturation measurements indicated that

(the lower limits to)  $|V_s|$  values decreased upon DCDC adsorption by 80 mV (from 220 mV to 140 mV) for the p-type samples and by 140 mV (from 580 mV to 440 mV) for the (type I) n-type samples.

Compared to the relatively large effect of DCDC adsorption, the effect of DHDC adsorption was much smaller. Only minor changes in the surface state energy levels deduced from SPS were found after DHDC adsorption.  $|V_s|$  values decreased upon DHDC adsorption by only 10 mV for the p-type samples and only 90 mV for the (type I) n-type samples. In a reference experiment with a blank acetonitrile solution  $|V_s|$  was reduced by 50 mV for n-type (type I) and no change was observed with the p-type samples. Additional experiments of DMDC adsorption on the p-type sample yielded no changes in  $|V_s|$ .

The effect of DCA adsorption on type II n-type samples was much smaller than on type I samples. CPD spectra of the bare type II surface (not shown for brevity) exhibited a higher density of surface states than that found in type I surfaces<sup>[25]</sup> and showed only minor changes upon adsorption of all DCAs studied, including DCDC.  $|V_s|$  values decreased by only 60 mV, 60 mV, and 80 mV, upon adsorption of DCDC, DHDC, and DMDC, respectively.

In agreement with earlier work of ours, we find that adsorption of the molecules also modified the samples' electron affinity. That effect scales with the molecular dipole and can be used to tune the band energy positions relative to vacuum. A detailed discussion of that effect can be found in the literature.<sup>[17,21]</sup>

To rationalize the experimental data, we plotted approximate band diagrams of the *bare* surfaces of the different samples studied, with respect to the LUMO energy levels of the DCAs *before* adsorption, shown in Figure 2a. These diagrams were constructed by:

- using the surface work function value extracted from the CPD measurements in the dark to calculate the position of the surface Fermi level with respect to the vacuum level,
- using the measured  $V_s$  value as an estimate of the surface band bending, and
- calculating the energy difference between the Fermi level and the band edges from the bulk doping densities.

The surface-state energy levels were extracted from the SPS data and the LUMO energies of the various DCA molecules were found as described previously.<sup>[17]</sup> The close agreement in the

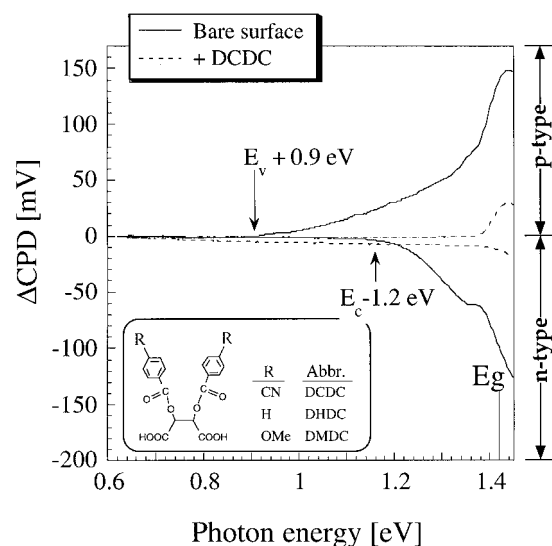


Fig. 1. CPD spectra of (type I) n- and p-GaAs(100) surfaces before (solid line) and after (dashed line) adsorption of DCDC. Inset: Schematic structure of the substituted dicarboxylic acids.

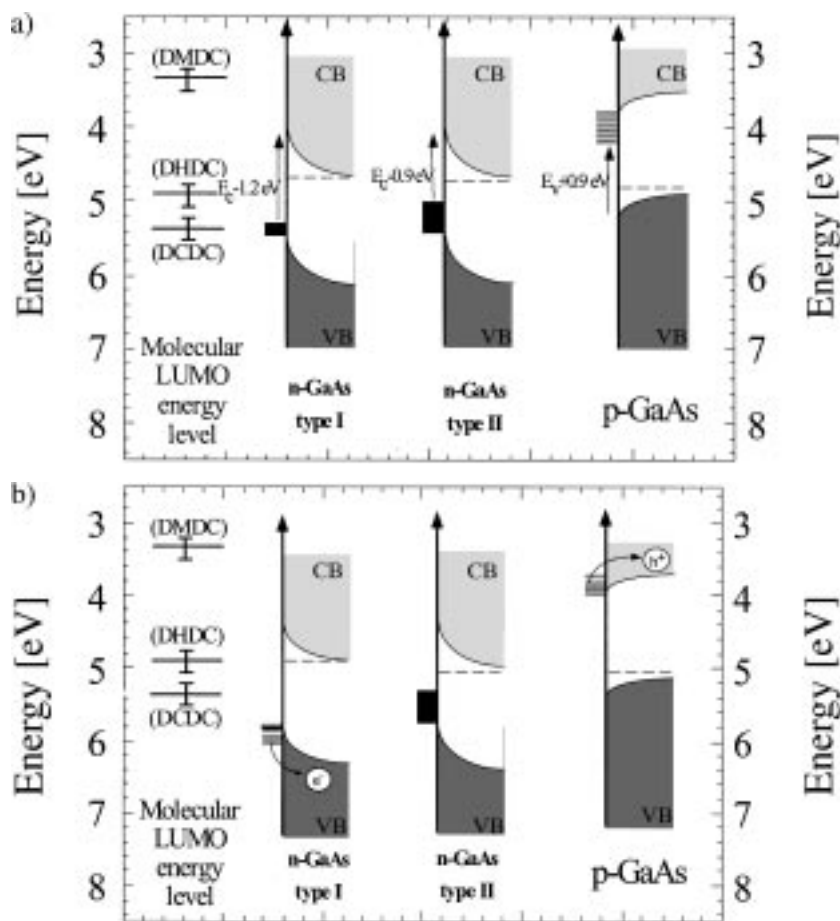


Fig. 2. Approximate band diagrams of a) bare, and b) DCDC-adsorbed (type I) n- and p-GaAs surfaces, with respect to the LUMO energy levels of the DCAs *before* adsorption [17]. Band edge values were obtained from contact potential difference measurements in the dark and under photosaturation. Surface-state energy levels were deduced from the SPS data. Arrows denote the major sub-bandgap transitions. ( $E_c - E_F$ ) values are  $\sim 10$  and  $\sim 60$  meV for type I and II n-type samples, respectively, and ( $E_F - E_v$ ) is  $\sim 90$  meV for the p-type samples. Surface states in and outside the forbidden gap are shown schematically as thick and thin lines, to indicate the difference in their surface localization [26].

energy position of the CB and VB edges (shift of  $250 \pm 50$  meV) fulfills our initial requirement that the bare surfaces studied should exhibit a similar surface potential. In Figure 2b we show similar band diagrams constructed for the DCDC-adsorbed surfaces. Comparing Figures 2a and 2b, we observe that the two main differences between the effect of DCDC on n-type and p-type surfaces are opposite shifts of the band edges and of the dominant surface state energy levels (both move down in n-type samples, up in p-type samples).

As explained above, in a generalized acid–base picture the surface charge should become more positive or more negative in both n- and p-type samples after the molecular treatment.<sup>[18]</sup> We further recall that the surfaces of n- and p-type samples are oppositely charged. Therefore, the absolute value of the surface charge, and hence the surface band bending, should increase for one doping type and decrease for the other. This prediction is contrary to the experimental observation of band-bending reduction in samples of both doping types. In addition, the DCA-dependent changes in  $V_s$  upon adsorption demonstrate that the degree of passivation depends on the nature of the molecule (i.e., on the substituent effect), even though the molecules have a similar binding group and bind in the same way to the surface.<sup>[20]</sup> This rules out the applicability of simple surface passivation arguments based on the filling of dangling bonds.

We now show that a HOMO–LUMO type of interaction between the surface states and the molecular orbitals does explain the experimental data, mainly the opposite shift in the energy of the surface states for the n- and p-type surfaces, consistently. An energy band diagram for the suggested interaction of DCDC with n-GaAs surfaces is shown in Figure 3a. We recall that at n-type surfaces the surface is negatively charged and the dominant surface states are filled, i.e., are analogous to HOMO levels. The molecular LUMO level interacts with the surface state levels and “pushes them down” in energy into the VB. This is reflected in the SPS data (see Fig. 1) by a shift of the sub-bandgap transition towards the VB edge. The states that are now in the VB continuum possess only a partial degree of charge localization at the surface (they are called “surface resonances”<sup>[26,27]</sup>) and thus will contribute much less than before to the surface charge. At the same time, the LUMO level is destabilized and is pushed upwards in energy close to the CB. As the total density of states inside

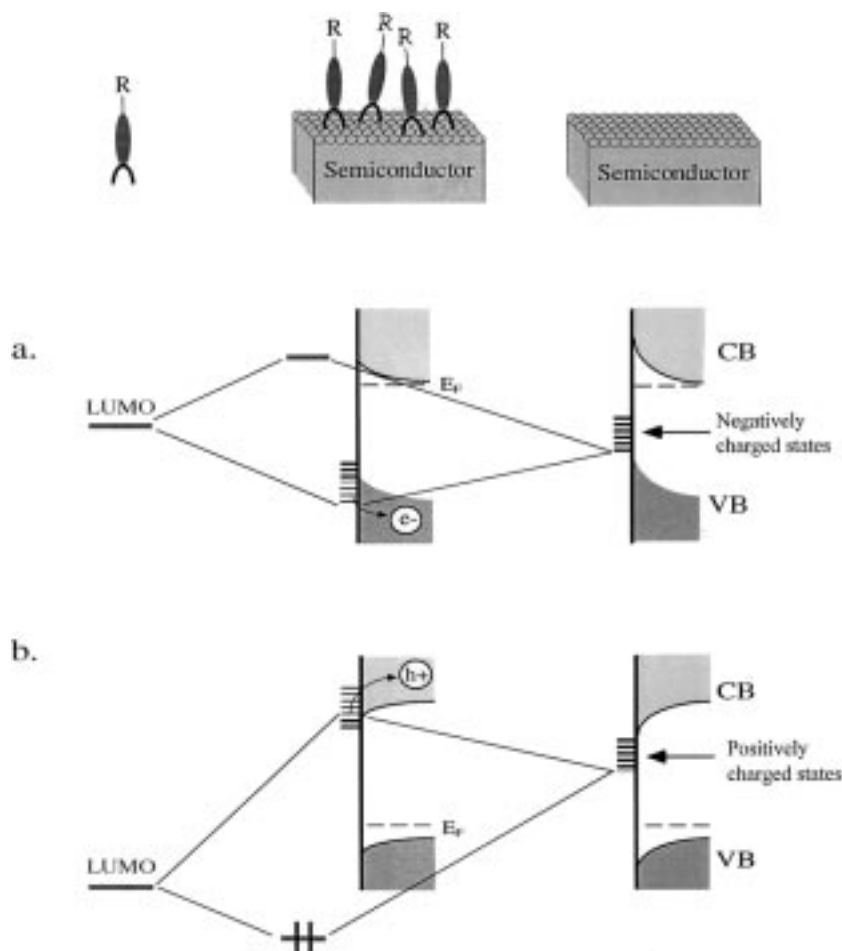


Fig. 3. Schematic energy level diagrams for the orbital interaction mechanisms of DCDC with the shallow surface states of GaAs: a) (type I) n-GaAs, b) p-GaAs. Surface states in and outside the forbidden gap are shown schematically as thick and thin lines, to indicate the difference in their surface localization [26].

the bandgap is reduced, fewer states are now available for charge localization. Therefore, the net surface charge, and hence also  $|V_s|$ , is reduced. Considering now DHDC and DMDC, which are molecules with less-negative LUMO levels (see Fig. 2, left), the energy difference between the LUMO level and the surface states is increased, the orbital coupling is reduced, and so is the interaction energy. Therefore, the surface-state energies are not shifted as much and the molecule’s ability to decrease  $|V_s|$  is diminished.

An energy band diagram for the suggested interaction of DCDC with p-GaAs surfaces is shown in Figure 3b. We recall that at p-type surfaces the surface is positively charged and the dominant surface states are empty, i.e., are analogous to LUMO levels. Therefore, at first sight we do not expect to observe a HOMO–LUMO interaction. Indeed, both DMDC and DHDC induce negligible changes in  $|V_s|$ .<sup>[28]</sup> However, in the case of DCDC, the LUMO level is more negative than those of DHDC and DMDC, relative to the p-GaAs surface Fermi level. Therefore, it can become occupied via orbital interaction and assume a HOMO-like character, with the empty surface states as-

suming a LUMO character.<sup>[13]</sup> In this case, the surface states are pushed towards less-negative energy, i.e., into the CB (where they can localize positive charge only to a limited extent<sup>[26,27]</sup>), which again reduces the total density of localized surface states, and thus  $|V_s|$ . In addition, the molecule, via its HOMO-like character, partially localizes negative charge on the surface upon adsorption, which again is expected to reduce the net positive surface charge and therefore  $|V_s|$ . Thus, the opposite nature of DCDC-induced changes in n- and p-type samples is rationalized.

A HOMO–LUMO interaction mechanism also explains adequately the differences between type I and type II n-GaAs surfaces. The type I surface exhibits a lower surface-state density and a stronger reduction in  $|V_s|$  is observed upon DCDC adsorption. A similar surface-state density effect was also found for differently doped n-CdTe crystals.<sup>[29]</sup> However, arguments based on the total surface-state density and on the molecule surface area and the density of the resulting monolayer cannot be used to explain the difference in  $|V_s|$  changes for the following reason. Let us consider an estimated “footprint” of DCDC of 40 Å<sup>2</sup> per molecule ( $2.5 \times 10^{14}$  molecules/cm<sup>2</sup>) and a surface-state density of about 10<sup>12</sup> cm<sup>-2</sup>. If each molecule interacts with one state, we would expect complete passivation,<sup>[18]</sup> which is not evident experimentally. Thus, we can conclude that other parameters, which in part are suggested by the above model, namely, the surface-state energy distribution and the mode of interaction (HOMO–LUMO), are equally important. Moreover, we can rationalize from the above arguments that imparting electronic effects to semiconductors can be achieved with even bigger molecules than the ones we used. This suggests that biological or specially designed multicomponent molecules can also be applied, as long as their molecular level(s) can interact efficiently with the surface.

In conclusion, we have shown that surface passivation due to the interaction of a given molecule with n- and p-GaAs surfaces is explained well by a HOMO–LUMO type of interaction between the frontier orbitals of the molecules and the semiconductor surface states. The observed electronic changes depend on the nature of the molecules, on the one hand, and on that of the surface states, on the other. Considering semiconductor surface passivation as a frontier orbital interaction mechanism should lead to its quantitative understanding, and use of such a model for designing molecular treatments of electronic materials thus provides a new tool for fine-tuning semiconductor device structures.

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