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Molecular Engineering of Semiconductor Surfaces and Devices

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ABSTRACT

Grafting organic molecules onto solid surfaces can transfer molecular properties to the solid. We describe how modifications of semiconductor or metal surfaces by molecules with systematically varying properties can lead to corresponding trends in the (electronic) properties of the resulting hybrid (molecule + solid) materials and devices made with them. Examples include molecule-controlled diodes and sensors, where the electrons need not to go through the molecules (action at a distance), suggesting a new approach to molecule-based electronics.

Introduction

The past decades witnessed a triumph of electronic materials in many practical applications ranging from computer components to solar panels, from laser materials to light-emitting diodes and flat panel displays. Until recently, these remarkable achievements relied nearly exclusively on a few families of semiconducting and metallic materials, composed of near-infinite networks of atoms, connected by so-called extended bonding.

While, ultimately, molecules may become alternative electronic device components, this will require overcoming such problems as addressing and contacting, and signal/noise of signals from single or small clusters of molecules. Until then, we should limit our expectations or increase at least some of the dimensions of the systems to be considered.

The structures of practical semiconductors and metals dictate many of their properties, and changing the solid's composition (e.g., via doping) to change its properties is possible only within certain, generally narrow limits, as the original structure needs to be preserved. It is therefore attractive to turn to the solid's surface to design materials with predetermined properties, via control over surface properties, because electronic transport through devices depends critically on the properties of the surfaces/interfaces through which electrons pass. By methods of chemisorption and self-assembly, one can "glue" organic molecules to semiconductor surfaces, to yield a hybrid system, a synergetic combination of the molecular and nonmolecular worlds.[1]

Grafting molecular properties onto semiconductors or metals allows use of the cooperative (electron transport) properties of these solids and the controllable functional versatility of molecules. Functions can vary, from chemical reactivity for recognition and, thus, sensing or physical protection (making surfaces hydrophobic, for example) to optical activity, if selective excitation of the molecules can change their interaction with the solid (cf. dye sensitization[2]).

Our approach to tune electronic properties of solids in a systematic and predictable way is based on modifying their surfaces with series of molecules, where within the series a given function is varied systematically (cf. Figures 1, 4a, and 6, inset). The reason is twofold. First, we can look for a systematic change of the hybrid (molecule + solid) system that corresponds to the variation in molecular property. This obviates the need for problematic quantitative comparisons between the free solid and the molecularly modified one. Second, we can tune the properties of the resulting hybrid systems. Once we understand the molecular effect, this can serve to analyze chemical events in the surface-bound molecules (molecular sensing) and to tune electronic device performance, as we showed recently,[3−5] thus leading to generic molecule-controlled electronic devices.

The following steps are involved in forming hybrid systems:

(a) Design and synthesis of a suitable series of at least three or four molecules, with systematically varying function and fixed skeleton, able to bind to the target surface.[6] We do so by utilizing molecules with identical surface binding groups and varying a substituent on the molecule, situated well away from that binding group.

(b) Finding experimental conditions, in terms of preparation of the solid surface and reaction conditions, for chemisorbing the molecules onto the solid. This can be checked by FT-IR, contact angle, and ellipsometry measurements.

When (a) and (b) are accomplished, characterization starts, to see if the desired change in property was, indeed, achieved.

In the following we separate solid-state basics from the molecular chemistry, so as not to discourage the different

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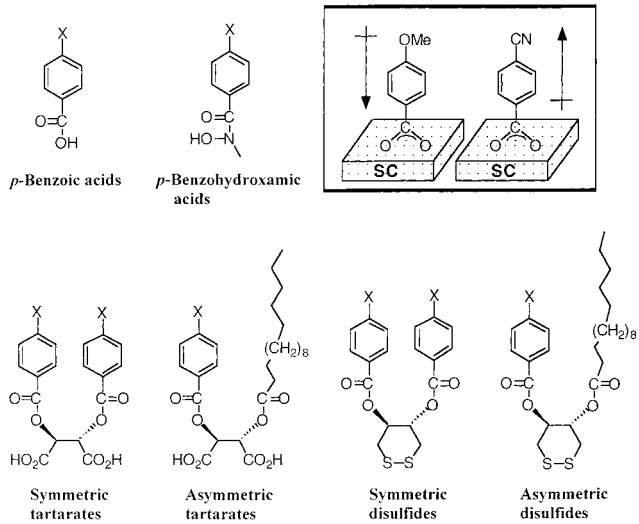

FIGURE 1. Structures of organic ligands that are used to modify systematically solid surface properties. The para(X) positions can be substituted by different functional groups that dictate the dipole moments of the entire structure. The inset shows two *p*-benzoic acid derivatives, with two extremes in dipole moment, as they are adsorbed on a semiconductor surface. The direction of the dipole is taken to be positive if the positive pole is directed toward the semiconductor surface. Additional ligands are shown in Figures 5 and 6.

readerships at which this Account is aimed, including both materials researchers and (in)organic chemists.

Ligand Design

In principle, molecules can be chosen from all commercially available ones. In practice, this limits severely the choice of functional groups. Therefore, we also synthesize ligands (Figure 1). Each ligand contains two distinct domains: (i) a surface binding group, the *anchor*, that facilitates chemical interaction between the molecular monolayer and the surface,[6] and (ii) a headgroup containing the functional element that varies the desired molecular property. Complementary approaches, which can improve our understanding of solid surface/organic ligand charge interaction, utilize series of molecules with systematically differing surface binding.[7]

For the *p*-benzoic, *p*-benzohydroxamic, and (bis-*p*-benzo) tartaric acid derivatives, 5 mM solutions suffice to saturate semiconductor surfaces, which are air-oxidized, as we work mostly in ambient atmosphere.[8] FTIR showed that adsorption proceeds via binding of the carboxylic groups to exposed cations on the semiconductor surface (e.g., Ga on GaAs or Cd on CdTe surfaces). The results suggested that the carboxylate binds as monodentate to Ga and as bidentate to Cd.[8,9] Different binding groups serve to attach molecules to Si, alkenes or alkynes to hydrogenated surfaces,[10] and silanes to oxidized Si.[11−13]

Coupling 2 equiv of the benzoic acids to tartaric acid bases yields the symmetric tartarates, shown in Figure 1. Their dicarboxylic acid anchor binds much stronger to semiconductor surfaces ($K_{GaAs} \approx 10^6$ M^{-1})[14] than the benzoic acids ($K_{GaAs} \approx 10^4$ M^{-1}).[9] Binding of the latter is described best as a "one-site" adsorption process, while a "two-site" mechanism fits best for dicarboxylic acids.[14]

Analysis of binding of disulfide anchored ligands (Figure 1) to semiconductor surfaces is helped by comparison to results on Au. In this way, effects of structural parameters of the monolayer, such as coverage and tilt, on the magnitude of the modification of surface properties could be taken into account.[15]

Introducing electron-donating or electron-withdrawing functional groups as para-substituents on the phenyl fragments varies the dipole moments of the entire molecule. The dipoles point to or from the surface, on which the ligands are adsorbed (Figure 1, inset). Varying the substituents changes the benzene fragment dipoles, from −1.5 D with an electron-donating group (*p*-methoxy) to ∼ +4 D with an electron-withdrawing group (*p*-cyano). Such tuning changes the electrical potential of the solid surface over a large range (see below).

The disulfide and tartarate ligands have a C−C bridge between their two arms that prevents chain segregation. In this dipodal configuration, both symmetric and asymmetric molecules can be prepared (Figure 1). A para-substituted benzyl and an alkyl chain were introduced simultaneously into the latter ligands. To a first approximation, monolayers made with "asymmetric" ligands are only half as dense in terms of functionalized benzyl groups, enabling incremental addition of dipoles relative to the dibenzyl molecules. Because of the long aliphatic chain, they are more hydrophobic than the symmetric ones with two benzyl groups.[15]

Molecular Control over Surface Properties of Semiconductors and Metals

Theoretical Considerations. While in molecules bonding is usually localized, in common solid-state electronic materials, which are nonmolecular, bonding *extends* over many atoms, and we can use the concept of "free" electrons in *delocalized* orbitals. While electrons in molecules occupy *discrete levels*, separated by energies many times the thermal energy, kT, in common semiconductors and metals the separation between electron energy levels is $\ll kT$, leading to quasi-continuous energy bands. Just as in frontier MO theory we focus on the HOMO and LUMO, here attention centers on the valence[16] and conduction bands (VB, CB).

Figure 2 shows the energy band diagram for an n-type semiconductor and associated electrical surface properties. The presence of dipoles or charge (monopoles) on the surface determines the *work function* (WF), the minimum energy required for an electron to escape into vacuum from the Fermi level (E_F) of the material.[17] The WF is determined by several factors (Figure 2):

(i) electron affinity (EA), the energy needed to bring an electron from vacuum just outside the semiconductor to the CB bottom at the surface;

(ii) band bending (BB), the electrical potential difference between the surface and the electrically neutral

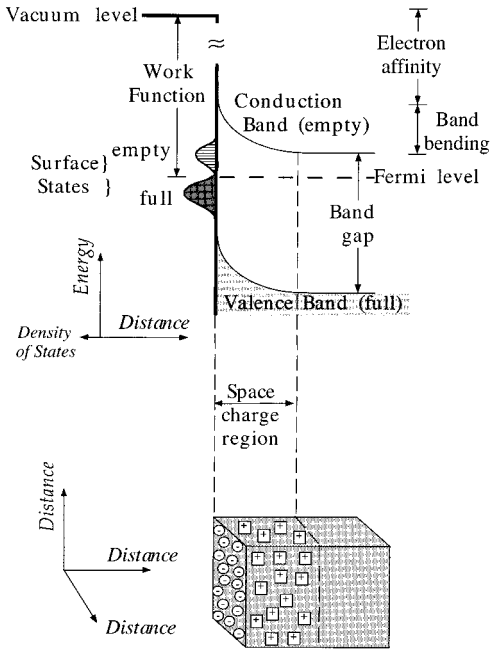

FIGURE 2. (Top) One-electron energy level diagram of n-type doped semiconductor. Vertical axis, energy; horizontal axis, distance into the semiconductor. The surface states are occupied until sufficient space charge is created in the semiconductor, corresponding to an electrostatic field, which prevents further electrons from going to the surface. It is this field that causes the shift in the band energies. (Bottom) Side view of the crystal. The surface localizes electrons and is negatively charged.

semiconductor bulk, often called the *built-in potential*, expressed in the band diagram by bending the CB and VB; and

(iii) the energy difference between the Fermi level and the CB in the bulk.

In the following section we show that the WF of a semiconductor/molecular layer hybrid can be changed by molecular dipoles, via changes in the EA. This is done by using molecules that do not induce significant changes in the surface BB. We then demonstrate the ability to simultaneously tune the EA, by molecular dipoles, and the BB, by matching the MO energies of a chosen molecule with discrete energy levels in the semiconductor band gap. Control over these two fundamental properties is the main tool to tailor the performance of electronic devices, as will be described in the last two sections.

For the systems considered here, the WF and EA are easily determined using the so-called Kelvin probe (KP) setup.[18] A flat plate capacitor is used, one plate of which is the sample and the other a vibrating grid of a reference material, usually Au. The WF difference between any two materials is their contact potential difference (CPD). The KP measures the CPD between sample and reference surfaces. Changes in WF (due to chemical treatment of the surface) are determined, assuming a constant WF for the reference. ΔWF can be due to ΔEA, ΔBB, or both, i.e.,

$$\Delta\mathrm{WF} = \Delta\mathrm{EA} + \Delta\mathrm{BB} \qquad (1)$$

For semiconductors, illuminating the sample with light with energy larger than their band gap ($h\nu > E_G$) and of sufficient intensity can practically neutralize the built-in potential and thus remove the BB. Since the CPD is measured relative to E_F and this is fixed with respect to the bulk VB and CB,[19] the light-induced change in CPD (the surface photovoltage, SPV) gives a lower limit for the BB. The EA is then extracted from the CPD under illumination, up to a constant, the energy difference between E_F and the bulk CB/VB, plus any uncertainty in the reference's WF.[20]

Tuning the Electron Affinity by Molecular Dipoles. The EA of a given surface is directly affected by any surface dipole. Thus, it can be modified dramatically following adsorption of molecules, as was shown for CdTe and CdSe single crystals, and for solar cell quality thin films of CdTe and $CuInSe_2$ using benzohydroxamic and *p*-benzoic acids.[8,21,22] The WF changes, due to modification by the different ligands and relative to bare surfaces, correlated linearly with the dipole moments of the substituted benzyl groups (without the acids), and with Hammett parameters of the para substituents. Both parameters reflect the electron-withdrawing or -donating power of the substituents. Hammett parameters were used earlier as a qualitative indicator for molecular modification of CdSe surfaces (cf. ref 1).

As summarized in Figure 3 for various semiconductor surfaces this linear correlation was found to be a general phenomenon. The concept was extended also to oxidized GaAs (100) surfaces. This is noteworthy because of the importance of GaAs and related materials for devices (see below) and because such surfaces are notoriously difficult to control in air. Apparently, the strong chemical binding of molecules stabilizes the surface.[9] Similar results were obtained on oxidized Si, using silane binding groups.[11]

Can we get larger and larger effects by increasing the molecular dipole? There are good (electrostatic) reasons why this is probably not so, and experiments to test this are under way in several groups. In an older experiment, we compared 3,5-dinitro- with *p*-nitrobenzoic acid on CdSe, to show that there is no linear additivity of WF changes, as a result of multiple polar substituents.[22]

Changes in WF depend not just on the molecular dipole moments, but also on the surface coverage by the active molecules and on their tilt relative to the surface normal (θ). The electrical potential drop, ΔV, across the molecular film can be expressed by

$$\Delta V = N\mu \cos\theta / \epsilon\epsilon_0 \qquad (2)$$

where N is the molecular density, μ the molecular dipole moment, ϵ the effective dielectric constant of the molecular film (which can be expressed in terms of molecular polarizabilities),[9] and ϵ_o the permittivity of free space. The inset to Figure 3A shows a linear relationship between the semiconductor lattice parameters and the $\Delta\mathrm{EA}/\Delta(\mu)$ slopes extracted from Figure 3A. This indicates that the lattice structure dictates the surface coverage, probably via the density of the exposed ions to which the molecules can bind (N in eq 2), and thus the magnitude of ΔEA that can be induced by the different substituents. In view of the fact that air-exposed, oxidized surfaces are used, this

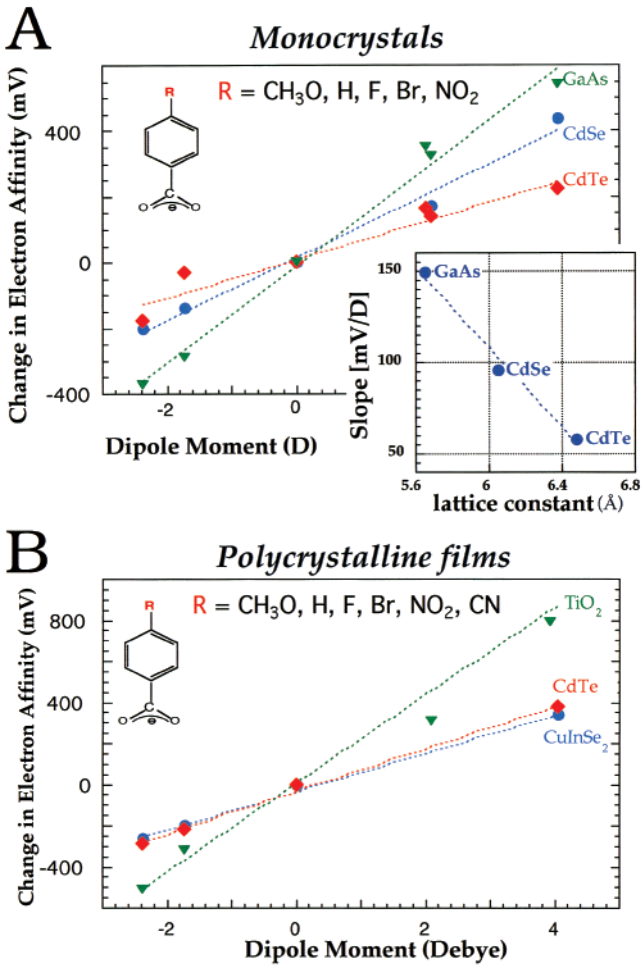

FIGURE 3. Plots of change in EA of several single-crystal and polycrystalline semiconductors upon molecular modification vs the dipole moment of the benzoic acid molecules adsorbed on their surfaces. EA values are relative to the bare surface values (shown as point (0,0)). Molecule binding was verified by FT-IR. Monolayer formation was followed by contact angle and, where possible, ellipsometry.[8,9,15,22,35] Inset: (Effective cubic) lattice parameters of the single crystals vs the slopes of the linear plots of (A).

sensitivity is remarkable. Similarly, peptide binding from aqueous solution to GaAs was found to be sensitive to the crystallographic orientation of the air-exposed surface.[23]

Equation 2 was tested in a comparative study, by assembling disulfide ligands (Figure 1) on both $CuInSe_2$ and gold surfaces.[15] In the Au experiments, which significantly extended earlier work,[24] the molecules' average tilt (~50°) and coverage could be determined, combining experiments and modeling. An excellent fit was found between what was calculated from eq 2 (right-hand side) and what was measured experimentally. For $CuInSe_2$ a reasonable fit was obtained, considering mainly the much lower coverage on this much rougher surface and higher tilt, as well. In other work, differences between results obtained with totally vs partially conjugated molecules were ascribed to changes in ϵ.[5] These results suggest that eq 2 has predictive power; i.e., it can be used as a guideline for designing molecules.

Molecular Control over Built-in Potential: Band Bending. The changes in WF due to adsorption of benzoic- or benzohydroxamic acids or disulfide ligands were attributed fully to altering the semiconductor EA. However, such an interpretation could not explain changes in WF for surfaces derivatized by the tartaric acids (Figure 1). There appears to be stronger electronic interaction of semiconductor surfaces with tartarates than with single carboxylates. Such an interaction can change the built-in potential of the semiconductor (and thus the BB).

BB is governed by the net charge density, localized on the surface, which is determined by the position (with respect to E_F)[17] and density of energy levels inside the band gap on the semiconductor surface. These levels are associated with surface states (see Figure 2). In contrast to levels in the bands, those associated with surface states localize electronic charge. This localization charges the surface and generates an electric potential difference with respect to the bulk. Because CB and VB levels are electron energy levels, they will follow such a potential difference (BB in the band diagram; Figure 2). Surface states on n-type semiconductors localize negative charge, and the opposite holds for p-type. The importance of surface states stems from the fact that they can dominate charge transport across the surface, as traps or recombination centers for carriers, when that surface becomes an interface, with a contact, for example.

Except for charge trapping, surface states can serve as fast recombination centers of electrons and holes. This leads to surface recombination, in addition to bulk recombination, and to a reduction in the lifetime of the excited electron−hole pairs below their bulk lifetime. This effect, which is critical for the electron-transfer efficiency in electronic devices, is expressed using the so-called *surface recombination velocity* (SRV). Mostly, the SRV is determined by the surface states close to the middle of the band-gap where the probability for electron−hole recombination is highest. SRV values can be extracted from time-resolved photoluminescence (PL) measurements (cf., e.g., ref 25).

Changes in net surface charge due to molecular interactions with the surface can come about by a change in absolute density of the states and/or by changing their position with respect to E_F.[17] Such effects can be explained using a molecular orbital (MO) picture,[26] by viewing the localized surface state energy levels as the semiconductor's frontier MOs. There are two ways in which interaction with the appropriate frontier orbital of the molecule can lead to changes in surface charge:

(1) if the density of surface states with levels above E_F (empty states) or/and below E_F (filled states) is changed, and

(2) if some levels become equi-energetic with bands, so that electrons are most of the time delocalized, thus reducing surface negative charge.

Frontier MO−surface state interactions explained the effects of adsorption of tartarate molecules with different LUMO energies on the BB of n-CdTe(111) (Figure 4A). The LUMO energies were estimated, using Koopman's theorem, by extracting the lowest singlet HOMO−LUMO transition from UV−vis spectra and using literature values

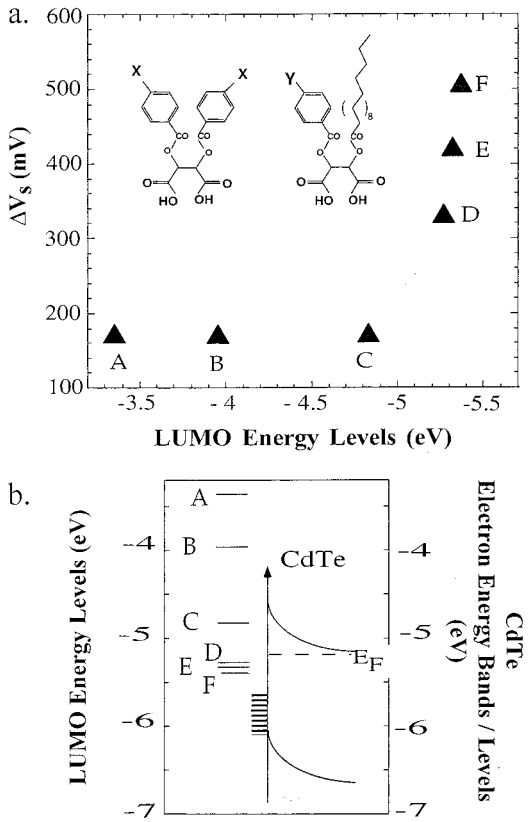

FIGURE 4. **(a)** Plot of change in BB (V_S) of n-CdTe upon adsorption of dicarboxylic acid derivatives vs LUMO energy of the benzyl substituents.[27] The following substituents were placed on the ligands: X = OMe (A), H (C), CF_3 (E), CN (F); Y = OMe (B), CN (D). **(b)** Energy diagram of bare CdTe (from Kelvin probe data) and of LUMOs of isolated molecules before adsorption. Axes as in Figure 2.

for ionization potentials (cf. discussion in ref 27). Besides n-CdTe, several other semiconductors were modified with the tartarate ligands. Conversely, for a given molecule, changing the semiconductor surface to n-CdSe(0001), n-InP(100), and n- or p-GaAs(100) led to changes in the molecular effects[25,27] in accordance with the MO interaction model. Further support for the model came from SPV and SRV measurements. The wavelength dependence of SPV gives information on the position of surface states in the gap. While changes in SRV indicate changes in surface state density near the middle of the band gap, changes in SPV indicate changes in states close to the band edges.[20,25,27]

The results provided some "design rules" for the selection of molecules to achieve control over semiconductor surface BB. The changes in BB upon adsorption of ligands stem from two main molecular contributions: a constant one due to the acid binding groups, and a variable one. The latter depends on the energy difference between the ligand's LUMO and the surface state levels. The smaller this difference, the stronger the molecule–surface state coupling, and consequently the larger the BB change (cf. Figure 4B). A further test of the model was to use the same molecular modification on both p- and n-GaAs surfaces. In contrast to expectations from a generalized acid–base model for molecule–semiconductor surface interaction, but in agreement with the MO picture, in both cases reduction of BB was observed.[28]

While EA changes depend linearly on the molecule's dipole moments, BB changes follow a *threshold* pattern, with the threshold occurring when the estimated LUMO levels cross the semiconductor Fermi level.[17] Whether this is coincidence or a general phenomenon awaits more extensive studies. We have limited our discussion here to the molecules' LUMO levels, as analogous interactions of HOMO levels with surface states did not appear to be energetically favorable. In cases where they are, interactions with them can also modify surface states and/or SRV.

Hybrid Sensors

The systematic control achieved by the use of organic ligands can be used to monitor the direct and indirect adsorption of chemical analytes. For this purpose a GaAs-based device, named a molecular controlled semiconductor resistor (MOCSER), is being developed as a sensor (by AMOS Ltd., with R. Naaman; Figure 5). It works by adsorbing molecules on a GaAs surface and measuring the change in current in a conducting GaAs channel, separated from the surface and molecules by an insulating film.[7] As a result of adsorption and/or chemical reaction of the adsorbed molecules, small variations in the electrical potential on the GaAs surface occur which can lead to considerable changes in free carrier concentration within the conductive layer. (The MOCSER differs from known "CHEMFET" or "ISFET" devices, where a gate or separate reference electrode is required. For a preliminary theory of the MOCSER's mode of action, see ref 29). This is expressed with high sensitivity in the change in amplitude or time dependence of the device current. We attribute the high sensitivity to its very shallow channel (~50 nm), constraining the carriers close to the (Al,Ga)-As/GaAs interface (Figure 5).

Molecules with chemical structures related to the bifunctional ligands in Figure 1 can be designed to include headgroups to bind functional fragments such as metal ions, small molecules, or even porphyrins. Figure 5 shows Fe^{III}–porphyrin complexes formed by such ligands, having dicarboxylic (or disulfide) anchors and imidazolyl headgroups that bind to the fifth and sixth coordination sites of metalloporphyrins.[30,31] We replaced the tartarate group by a malonate one, because the ester groups that linked the succinic acid-like anchor with its headgroups were too easily hydrolyzed in the presence of imidazoles. CPD and PL measurements of CdSe derivatized by these complexes show that the porphyrins connect well to the semiconductor surface via the intervening ligands.[32]

The imidazolyl residues in these ligands are bound to Fe^{III} or Mn^{III} in a kinetically labile fashion, so that one of them can be replaced by a stronger binding substrate that approaches the porphyrin. Monolayer assemblies made of such complexes bind O_2 reversibly.[32] Sensing events based on metalloporphyrin chemistry are communicated via the ligand to the solid support. The transduction

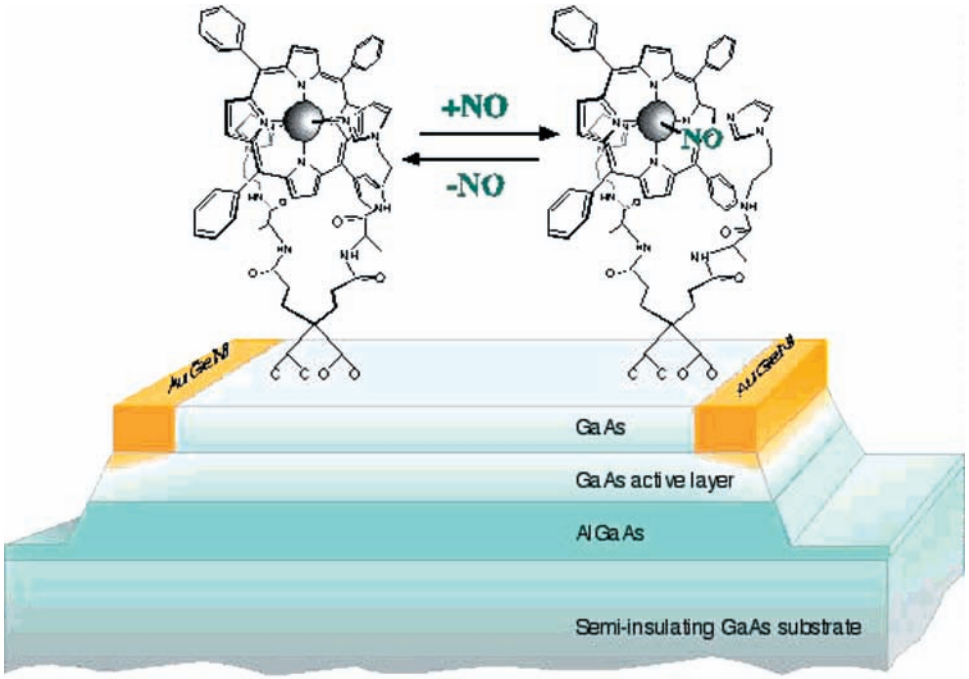

FIGURE 5. Schematic drawing of molecular controlled semiconductor resistor (MOCSER) device, with its surface derivatized by ligand–metalloporphyrin complexes, suitable for detection of NO. Current flows between the Au–Ge–Ni contacts to the GaAs active layer (n-GaAs), which is sandwiched between insulating GaAs and (Al,Ga)As layers. The electrical potential of the molecularly modified surface is such that current will flow only in a thin film very near the (Al,Ga)As/n-GaAs interface. As a result, even small changes in that potential (e.g., NO–porphyrin interaction) lead to measurable changes in current through the device.[7,14,31]

manifests itself as a change in the solid's surface electronic properties. By adsorbing ligands on CdSe, changes in surface potential can be followed via PL,[32,33] in agreement with earlier work.[1] Electroluminescence from commercial LEDs was used recently to sense gases such as ammonia and SO_2.[34]

MOCSERs derivatized by the ligand–metalloporphyrin systems (Figure 5) detect NO down to 1 ppm (~30 μM) and can follow NO binding in physiological aqueous solution (pH = 7.4, Figure 6). Improved response to NO resulted from improved signal transduction to the surface by replacing disulfide by the stronger binding dicarboxylic anchors (**2**, Figure 6, inset). Further improvement came by weakening the imidazolyl–metal interaction that needs to be broken by NO, using asymmetric ligands (**3**).[31] Use of native hemin, bound directly to the MOCSER GaAs surface through its carboxylates, enabled NO detection down to ~30 ppb.[29]

Engineering Electronic Devices by Molecules

Molecules can also control optoelectronic device characteristics. We modified diodes by adsorbing the tartarate ligands (Figure 1) onto single crystals of n-GaAs, followed by soft deposition of gold contacts on the modified surfaces.[3] Such deposition is important, as conventional contact deposition methods can damage the organic molecules. $I-V$ curves of series of modified Au/n-GaAs junction are shown in Figure 7. These show qualitatively that the organic monolayer increases the current if the molecular dipoles point away from the surface (e.g., CN derivatives) and decreases the currents for opposite dipoles (e.g., OMe), compared to the unmodified junction.

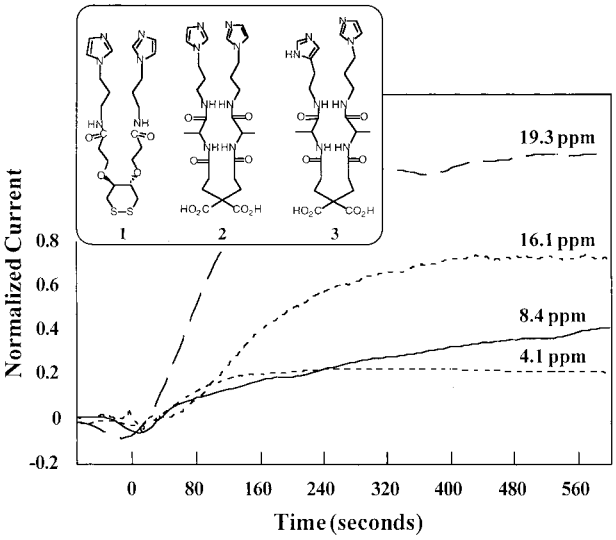

FIGURE 6. Changes in MOCSER current over time, due to exposure of a MOCSER, covered by the iron–porphyrin complex of ligand **1** (see inset), to different concentrations of NO in pH = 7.4 buffer solution.[31] Inset: Structures of ligands **1**–**3** that wrap around iron–porphyrins, bind to their fifth and sixth coordination sites, and link them to semiconductor surfaces. A MOCSER covered by complexes of **2** or **3** is more sensitive to NO than that covered by complexes of **1** (see text for explanation). As noted in the text, use of hemin improves sensitivity even further, down to 30 ppb.[29]

The modification in device current can be modeled as a change in effective barrier height for each diode. This parameter is influenced by the interface dipole, which correlates linearly with the ligands' dipole (eq 2). Because the GaAs WF can be modified linearly by varying the molecular dipoles of the adsorbed monolayer (as shown

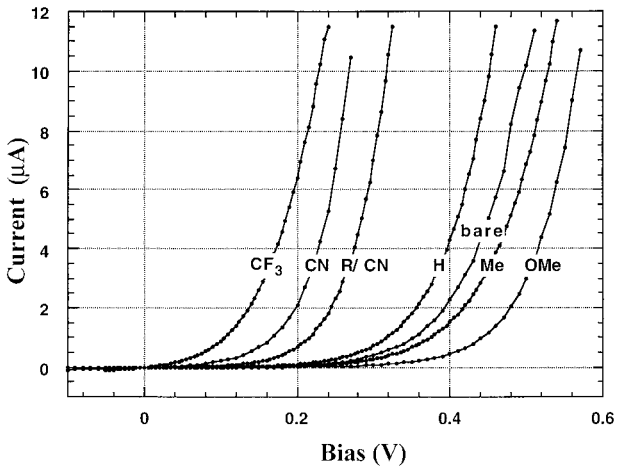

FIGURE 7. Current voltage (*I*−*V*) curves of Au/molecule-on-n-GaAs junctions, which differ from each other only by the substituents on the benzene ring of the tartarate derivatives (Figure 1). R/CN refers to the asymmetric tartarate having a long alkyl chain and a substituted benzyl (after ref 3). Similar results are obtained with a series of conjugated molecules.[5]

in Figure 3), one has a simple tool to test diode modification prior to its preparation. As is the case for molecule-free systems, only some 10% of the changes in the Au/semiconductor CPD are expressed as changes in effective barrier height.

A complementary configuration can be used, as well, where disulfide ligands (Figure 1) are adsorbed on Au, with which Au/SiO_x/Si diodes are made.[4] In these diodes the metal WF rather than the semiconductor's EA is changed. Results are opposite to those obtained with GaAs/Au diodes, because the substituted phenyl groups point in opposite directions in the two cases.

Considering the small molecules and rough surfaces used, the organic monolayers cannot provide perfect surface coverage, leaving pinholes, although less so with the better monolayers on Au than with those on GaAs. As a result, in our analyses tunneling needed to be taken into account for the Si/Au, but not for the GaAs/Au ones. In general, it can be stated that interfacial dipole effects are seen for incomplete, far-from-ideal monolayers, because the electronic carriers need *not* to pass, and most probably do not pass, through the molecules. Rather, the molecules affect the energy levels, involved in electronic transport, at both sides of the interface, relative to each other.

In related work, Krüger et al. used benzoic acids (Figure 1) to modify the *I*−*V* characteristics of TiO_2−organic heterojunctions.[35] Campbell et al. used self-assembled layers of conjugated thiol molecules to change the barrier height between a Cu electrode and organic electronic material used for LEDs.[36] Performance of the devices correlated with changes in the WF, which were controlled by the adsorbed ligands. In related work, it was shown that pretreatment of the transparent conductor In_2O_3:Sn with organic molecules significantly improved the characteristics of organic LEDs.[37] Molecular surface treatments have been used also for organic-based optoelectronic circuits. Improvement in charge mobility of a FET−LED device was demonstrated by using hexamethyldisilazane prior to deposition of the conjugated polymer.[38]

Solar cells are another field of applications for molecular surface functionalization. The tartarate molecules were located at the surface of the crystallites of a film of polycrystalline p-CuIn(Ga)Se_2, before making it into a solar cell, by depositing n-CdS onto it using a wet chemical bath.[39] Changes in *I*−*V* characteristics of the solar cells correlated with the molecules' dipole moments that modify the band line-up at the interface, rather than as a direct effect on the surface BB. The conclusion of this early work, supported now by more recent results,[3−5,35] is that device performance can be controlled by molecules that will modify the energetics at the interface so that any charge carrier passing from one side of the junction to the other will be influenced by it.

Conclusions

The studies described here indicate the tremendous potential of molecular treatments for tuning charge transfer and charge transport across (semi)conductor/semiconductor interfaces.

As more experience is gained and methods are developed to bind molecules and, in the case of actual diodes, to form contacts, more complex functions (catalysis, biocatalysis, biorecognition, and multiple switching based on recognition) will become possible. Where applicable, use of poly-[8,39] or even nanocrystalline semiconductors,[2,19] with their vastly increased surface area, can yield systems that are even more sensitive to molecular engineering than those described here. For some of these goals, multilayers that can hold more than one active molecule vertically[40] may be useful. In all these, relying on action at a distance, rather than on electronic transport through the molecules, appears important to bypass the stability issue.

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(6) Suitable binding groups for anchoring to target surfaces are carboxylic, hydroxamic, and phosphoric acids (for CdS, CdSe, CdTe, GaAs, InP, $CuInSe_2$, TiO_2, ITO), sulfides and thiols (espe-

cially for noble metals), and silanes (for SiO_2, Al_2O_3). Use of such groups allows self-assembly of molecules on the surface. Mostly this leads to only average order (imposed by the surface binding). With long-chain aliphatic molecules, well-ordered monolayers can form.

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(16) Abbreviations used: BB, band bending; CB, conduction band; CPD, contact potential difference; EA, electron affinity; E_F, Fermi level; HOMO/LUMO, highest/lowest (un)occupied MO; KP, Kelvin probe; MO, molecular orbital; PL, photoluminescence; SPV, surface photovoltage; SRV, surface recombination velocity; VB, valence band; WF, work function.

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