

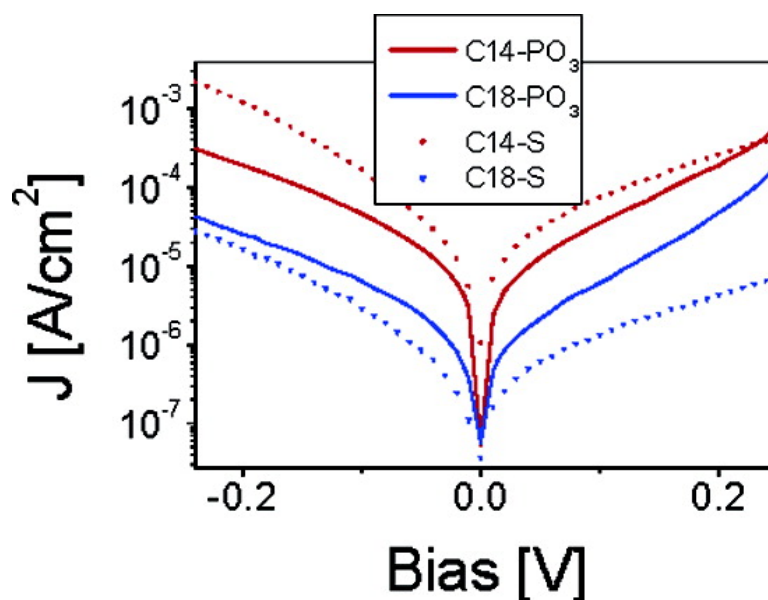
Communication

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Effect of Chemical Bond Type on Electron Transport in GaAs–Chemical Bond–Alkyl/Hg Junctions

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Does the way molecules are connected to an electrode affect electrical transport across these molecules, and if so, how? In principle several factors, such as changes in interfacial dipole moment, in electronic energy level position and density, in molecular orientation, and for monolayers, in their density, can affect the transport. To distinguish between the different effects it does not suffice to compare only raw transport data, but the experimental system should allow collecting sufficiently high-quality data for further analyses. For this purpose we prepared, characterized, measured, and compared transport through two metal–molecule–semiconductor junctions, with Hg as metal, n- or p-GaAs as semiconductor, and thiol or phosphonate alkyl chains of varying lengths as molecules, which bind via S–As or O–Ga bonds to the GaAs.

The very high surface tension of liquid metals limits the ability of Hg to penetrate into monolayer defects, including pinholes, thus avoiding shorting via pinholes.¹ As a result, excellent reproducibility can be achieved if the Hg surface is not contaminated by the ambient. We chose to use a semiconductor as one of the electrodes because it allows changing the electrode's work function without changing the nature of the chemical bond. We chose GaAs because the same molecules can be chemisorbed to its surface via different binding groups.² As shown in Figure 1, there is a clear difference in electron transport between the two systems, p- and n-GaAs.

GaAs surface preparation was identical for thiol (system **1**) and phosphonate (system **2**) adsorption, with only the solvents for adsorption of the molecules being different (cf. Supporting Information). This minimizes the possibility that differences in transport are due to factors other than binding to the GaAs or the resulting orientation and packing of the molecules between the GaAs and the Hg. The latter effects can originate from changes in the density of the monolayer, the film thickness, or the tilt angle of the molecules. To distinguish between the possible remaining factors, we used for both **1** and **2** alkyl chains with different lengths (binding group–(CH₂)_{n–1}–CH₃, referred to as C_n, with *n* = 12, 14, 16, 18, the number of the carbons in the alkyl chain). This not only isolates effects of mere monolayer thickness but also provides a basis for further data analyses.

Table 1 summarizes the results of our characterizations of the molecular layers on GaAs. Ellipsometry shows that the thickness of **1** is ~1.5 Å less than that of **2**. This difference can be traced directly to the difference in binding groups, because while in **1** only the S atom couples between the alkyl chain and the GaAs surface, in **2** coupling is via P–O which adds ~1.5 Å, assuming similar tilt angles of the alkyl chains on the GaAs surface for the two systems. The water contact angles show all samples in both systems to be very hydrophobic and dense. From the position of the antisymmetric vibrational stretch of the C–H bonds (on the alkyl chain), measured by FTIR, we can deduce that the alkyl chains are solid-like³ with a low density of gauche defects. The characterizations also show that in both systems monolayer quality improves with the number of methylene groups in the alkyl chain, as expected, because the longer the chains, the more van der Waals

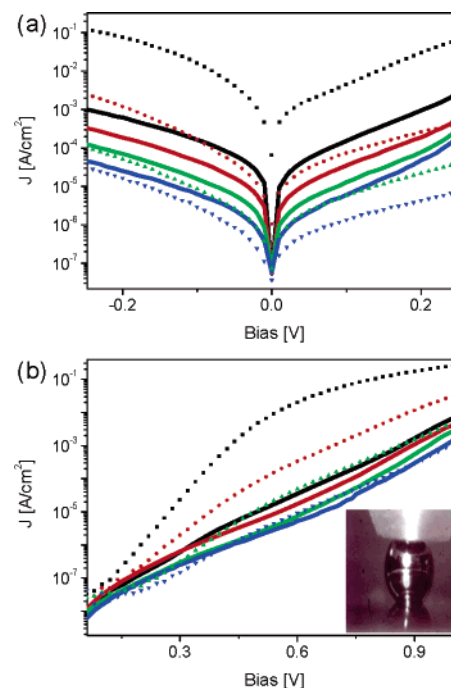


Figure 1. Experimental I–V curves for (a) p- and (b) n-GaAs–binding group–C_nH_{2n+1}||Hg junctions (*n* = 12, 14, 16, 18). Thiols (**1**): C12, black ■, C14, red ●, C16, green ▲, C18, blue ▼. Phosphonates (**2**): C12, black line, C14, red line, C16, green line, C18, blue line. Current density is shown as a function of the applied bias. Errors are 10%. (For the reverse bias data of **1b**, see Figure S1). Inset: Photo of Hg drop on, and its reflection in the sample.

Table 1. Characterization of Alkyl Chain Monolayers on GaAs with Different Molecule–GaAs Binding Groups: **1**, Thiol; **2**, Phosphonate¹¹

+monolayer system	ellipsometry thickness (Å) (±5%)		contact angle (deg) (±1°)		CH ₂ antisymmetric stretch peak position (cm ^{–1}) from FTIR (±0.05 cm ^{–1})	
	1	2	1	2	1	2
C12	14	18	110	113	2920.5	2919
C14	19	20.5	111	113	2918.5	2918.5
C16	21.5	23	112	114	2917	2917
C18	24	25.5	112	114	2917	2917

intermolecular interactions there will be and, therefore, the better the order in the monolayer. These experimental observations indicate that the alkyl chains in these two systems behave very similarly.

X-ray photoelectron spectroscopy (XPS) served to investigate the interface between GaAs and the molecular layer. In a recent XPS study for **1**^{2f} we showed that an As–S bond formed and that the density of low oxidation state Ga atoms is comparable to the density of S atoms, indicating that Ga–O (probably hydroxyl groups) form alongside As–S bonds.

In **2**, the concentration of oxidized As and Ga species is 3 times that of P, in agreement with PO₃ as binding group. All oxidized Ga is in a low oxidation state, and its concentration is twice that of

P, which indicates that each molecule **2** forms two Ga–O bonds. However, there is also oxidized As in a high oxidation state (shifted ~ 3 eV from the main As_{GaAs} peak) at a concentration similar to that of P.

From these observations it seems that the main difference between the two systems is the bond that is formed at the interface between GaAs and the molecular layer. While in **1** this is As–S, in **2** it is Ga–O (forming a Ga–O–P link with the alkyl chain). How is this difference in bonding related to the difference in electron transport that is seen clearly in Figure 1?

To answer this question we refer to our recent report on the electrical transport characteristics for **1**,^{2f} where we showed that with p-GaAs transport is by tunneling, similar to what is observed for p-Si–C–alkyl/Hg junctions (Salomon, A.; et al. *Adv. Mater.* In press). The data in Figure 1a indicate that the same holds for **2** with p-GaAs, although the dependence on the width of the tunnel barrier is much smaller than for **1**. To understand this difference we analyze the p-GaAs data (cf. Figure S2) using the very simplified model of tunneling through a rectangular, homogeneous dielectric barrier. Within this model, tunneling is described by the width, d , of the dielectric, the distance between the electrodes, which we take as an experimental observable (cf. Table 1), by the tunneling barrier height, Φ_t , and by the effective mass of the carriers of that tunnel, m^* . The current is proportional to $e^{-\beta d}$, where $\beta \propto [m^*(\Phi_t - V/2)]^{1/2}$ with V the applied voltage.⁷ By applying this model to the two systems (plotting β^2 vs V) we find that for p-GaAs $\Phi_t = 0.8 \pm 0.3$ eV for **1** and 1.1 ± 0.3 eV for **2**, while $m^* = 1.5 \pm 0.3m_0$ for **1** and $0.3 \pm 0.1m_0$ for **2**, where m_0 is the electron rest mass. While m^* for transport through **2** is very similar to values deduced from tunneling experiments through alkyl monolayers on Au^{5a} and on Si,⁴ as well as to a theoretically predicted value for alkyls,^{5b} we are not aware of precedents for the high m^* for transport through **1**.

Analyses of transport and photoelectron spectroscopic data for **1** with n-GaAs^{2f} showed electronic transport through those junctions to be limited by thermionic emission⁶ over a barrier in the GaAs at low forward and at reverse bias, and by tunneling⁷ across the molecular barrier at higher forward bias. These results are similar to those we obtained for the n-Si–C–alkyl/Hg⁴ system and they agree with predictions for MIS junctions.⁸ Figure 1b shows that the behavior of **2** is somewhat similar to that of system **1**, but with a less pronounced transition between low and high forward bias and, as for the p-GaAs case, with a much smaller spread of currents.

For **1** at low bias thermionic emission dictates transport, while at higher bias the thermionic emission barrier is so much reduced that tunneling dictates transport. The Schottky barriers that can be deduced are quite similar, 0.85–0.89 eV with system **1** and 0.83–0.84 eV with system **2**, and the transition from thermionic emission to tunneling-dominated currents occurs at similar bias (~ 0.35 – 0.4 eV). The Schottky barrier explains why, with n-type junctions, tunneling-like behavior is seen only at high forward bias: only then will there be a significant potential drop over the molecules. In the tunneling regime, we applied the same simple model as that used for the p-type junctions and find $\Phi_t = 0.8 \pm 0.3$ eV for **1** and 0.7 ± 0.3 eV for **2** (cf. Figure S3). The effective masses are similar to those deduced from the p-type junction data, $1.5 \pm 0.3m_0$ for **1** and $0.3 \pm 0.1m_0$ for **2**. Thus, within the simple model used to analyze the transport data, the systems differ primarily in their effective mass values.

To understand the physical meaning of these observations we note that the tunneling current is affected by the interface in two ways: (1) Surface states are formed by the interaction between the molecules and the GaAs⁹ and may be further modified by the

Hg contact. The energy and density of these states will dictate the height of the average tunneling barrier, Φ_t . (2) The interface chemical bond can cause scattering of electronic carriers which can be expressed, in the model used here, in their effective mass, m^* .

Our results suggest then that the main difference in the electronic transport behavior of the two systems lies in the nature of the chemical bond. In **1** the alkyl chains are connected to the semiconductor via the relatively weak As–S bond, while in **2** this connection is via the much stronger Ga–O bond. This bonding difference is expressed primarily in the effective mass that, among other things, will reflect molecule–electrode coupling and, to a lesser extent, the barrier height.⁹ The strong Ga–O interaction apparently creates an electronic and electrostatic structure at the interface that leads to less scattering of the carriers that cross the interface than with the As–S bond. In the simple tunneling model that we use here this difference is then expressed as a smaller effective mass (in **2**). A possible explanation may be found in the observation that the As–S bond is rather unstable (as is the Au–S bond¹⁰). Possibly not all the S atoms are connected to As atoms, which would lead to (more) defects at the interface of **1** (than at that of **2**).

In summary the difference in transport through GaAs/binding group/Alkyl/Hg junctions stems from the interface between the GaAs and the molecular layer and can be attributed directly to the chemical bond that is formed there.

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Supporting Information Available: Experimental details and the results of the transport measurement analyses. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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