

Effect of Molecule–Metal Electronic Coupling on Through-Bond Hole Tunneling across Metal–Organic Monolayer–Semiconductor Junctions

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Electronic transport across all-trans alkyl chains is found to depend critically on whether the chains are chemically bound to the electrodes or not. We conclude this by measuring metal/molecule/semiconductor junctions of the type depicted in Figure 1. The p-type semiconductor, used here, allowed experimental verification of the theoretical prediction that tunneling of holes in these systems will be more efficient than that of electrons.¹ We actually find hole tunneling in σ -bonded chains to be similar to electron tunneling through conjugated ones.

The current, I , through saturated hydrocarbon spacers is predicted to obey the relation $I = I_0 e^{-\beta d}$, with d the distance through which tunneling takes place and β the structure-dependent attenuation factor for the molecules.¹ More efficient tunneling processes are described by lower β values.

Hg was used as the “soft” top contact so as not to damage the molecules.² The high quality of the pinhole-free monolayers of alkanethiols on Hg ensured reproducibility of the junctions.³ As Hg does not react with Si or SiO₂ surfaces,⁴ there was no need to use a bilayer of molecules. We stress that the measurements were *not* conducted in solution.

The continuous lines in Figure 2 form a typical set of I – V curves measured for alkanethiols of different lengths (junction **a** in Figure 1). The curves are quite symmetric around 0 V (see Figure 2, insert A), suggesting there is no significant barrier inside the semiconductor and that virtually all of the applied potential drops over the interfacial layer.⁵ This fits the similar work function values (± 0.1 V), that we derived from our Kelvin probe measurements of the SiO_x (on Si) and alkanethiol-modified Hg drop surfaces. This means that no substantial charge redistribution needs to occur upon junction formation.

The similarity in structure of alkanethiol monolayers on Hg³ to that of alkyl silanes on SiO₂⁶ allows us to test how a difference in the way these alkyl spacers contact the electrodes affects the I – V characteristics.⁷

n-Alkyltrichlorosilanes ($n = 12, 14, 18$) monolayers were deposited on SiO_x/p-Si at 4 °C, using procedures, known to give densely packed monolayers with highly ordered aliphatic chains.⁶ The I – V curves of the resulting **b** junctions, shown in Figure 2 as open circles, show, in contrast to the clear chain-length dependence found for the alkanethiols, no significant differences between the different silanes. The difference in current between C₁₂ and C₁₈ is less than an order of magnitude. This surprising result agrees with the lack of, or weak dependence on, alkyl chain length, found for currents across *n*-Si/SiO_x/alkylsilane/metal⁸ and *n*-Si/SiO_x/liquid electrolyte junctions,⁹ respectively. These differences between Hg-thiol-based **a** junctions and the silane-based **b** junctions suggest that the latter cannot be described by the simple tunneling model that fits the **a** junctions. We postulate that the cause for this

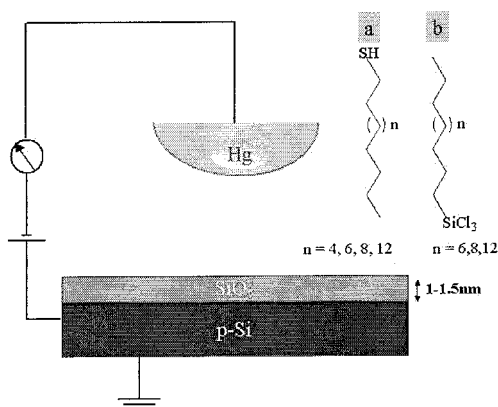


Figure 1. Schematic description of the junction and molecules used in the experiments. Junction **a** consisted of alkanethiols adsorbed on the Hg; junction **b** consisted of alkyl silanes assembled on the SiO_x/p-Si.

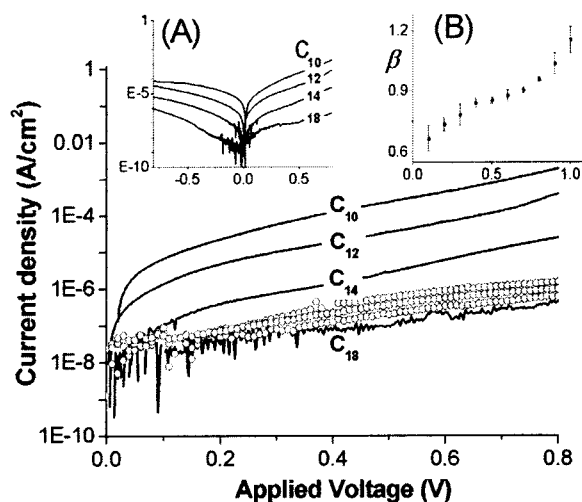


Figure 2. Experimental I – V curves for Hg/alkyl chain/SiO_x/p-Si junctions. (—): **a** junctions of alkanethiols on Hg. (○): **b** junctions of C₁₂, C₁₄, and C₁₈-alkyl silanes on SiO_x/p-Si. As we use p-semiconductors, at forward bias ($V > 0$) Hg is negative with respect to the p-Si; in reverse bias ($V < 0$) the situation is opposite. INSERTS: (A) Roughly symmetric behavior of I – V curves for junctions **a** around 0 V. (B) Dependence of β in **a** type junctions (with alkanethiols on Hg) on the applied voltage.

unexpected behavior is that the silane *alkyl chains are to a large extent decoupled from both electrodes.*

The procedure for alkyl silane assembly requires the temporary presence of an ultrathin, interfacial water film on the substrate. This layer is thought to allow the formation of a highly organized, transient Langmuir-type film of hydrolyzed silane molecules, which then form the final polymerized film by compliant cross-linking of the siloxy network. The substrate-bound water promotes decou-

pling of the organic film from the underlying solid surface. As a result, for highly dense monolayers, insignificant bonding exists between the alkylsilanes and SiO₂.⁶ These monolayers can be viewed as networks of interconnected alkyl chains, which are covalently tethered to the electrode at very few points.

If we assume that coupling to the Si side of *both junctions*, **a** and **b**, is negligible, the difference in their behavior results from differences in the way the molecules contact the Hg. Assuming through-bond tunneling,¹ the S–Hg chemical bond will be critical for the charge-transfer process. Without it (junction **b**, with silanes), the density of states and the potential distribution across the junction are changed, yielding a potential energy barrier for electronic transport between the alkyl chains and the metal, which becomes dominant in the over-all charge-transfer process. Temperature-dependent studies with a different setup are in progress to study this.

The above results suggest that, in the absence of a chemical bond between the alkyl chain and the metal, not only is the conductivity lower, but the charge-transfer mechanism is also changed.¹⁰ Further work is needed to understand this change. Nevertheless, we are still able at this stage to draw some interesting conclusions regarding the tunneling mechanism through the thiol-based **a** junctions. Use of p-Si assured hole tunneling across the junction, which was predicted to be more efficient than electron tunneling, in this case.¹ However, no experimental evidence based on a molecular solid-state device has been presented thus far to test this prediction.

Using data measured for junctions **a** between 0.0 and 0.1 V (see below, why) we find β to be $0.65 \pm 0.08 \text{ \AA}^{-1}$. It is lower than experimentally reported β values for *electron* transfer through σ -bonded chains, which range from ~ 0.8 to 1.0 \AA^{-1} . On the basis of this, hole tunneling through all-trans alkyl chains is indeed found to be more efficient than electron tunneling. Such low β values are comparable to values for electron tunneling through highly conjugated molecules,^{2c} suggesting that hole tunneling through σ -bonded systems is as efficient as electron tunneling through π -bonded ones, as previously predicted.^{7c} The result is nevertheless higher than calculations in an earlier ab initio study^{1c} ($\beta \approx 0.1 \text{ \AA}^{-1}$) that predicted weak distance dependence of through-bond hole tunneling over distances larger than $>21 \text{ \AA}$.

The agreement of the experimental β value with theory is the more important because the theoretical predictions for hole tunneling ($\beta = 0.4\text{--}0.8 \text{ \AA}^{-1}$) were based on free molecules. Our results suggest that these predictions hold also when the molecules are connected to surfaces.

β appears to increase as a function of voltage (Figure 2, insert B). We view this behavior, which has not been observed before, as experimental proof that through-bond tunneling is most efficient in an all-trans conformation.¹¹ β for through-bond tunneling is expected to increase once defects are formed in an all-trans configuration of an alkyl chain. As the bias increases, a progressively larger electrostatic force acts on the monolayers (the pressure can be as high as tens of atm; cf. refs 2a,d). As a result, several defect-producing processes that decrease the efficiency of tunneling (increase β), can occur simultaneously: (i) formation of gauche conformations, destroying the all-trans configuration, (ii) cooperative tilting of domains in the monolayers, increasing through-space tunneling probability (interchain hopping) which was shown to be less efficient than through-bond tunneling,³ (iii) partial alkanethiol desorption from the negatively charged Hg surface, lowering molecule–metal coupling and the tunneling efficiency across the

interface. We extract β values only at low bias values, before any defect-producing processes take place.

As is clear from comparing junctions **a** with **b**, alkyl chains can be good hole conductors (comparable to conjugated systems as electron conductors) as long as the chains are chemically bonded to the contacts. In the absence of such bonds they behave effectively as insulators. We can draw these conclusions because we use monolayers (of alkanethiol on Hg and alkyl silanes on Si/SiO₂) that are of comparable quality (based on separate contact angle measurements). The key point is that the monolayer structures in both cases are the same, to a first approximation. The comparison that can thus be made illustrates *experimentally* that understanding of, and chemical control over, the molecule–metal interface is crucial to molecular (i.e., molecule-based and -aided) electronics.

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- (10) Our results support and compliment the recent ones of Cui et al. (ref 7g), who observed a strong effect on *I–V* characteristics due to absence of chemical bonding of a single molecule to a metal contact. It may very well be that also in their case there is a change in transport mechanism, but as only one given length of molecule was used, this is hard to say.
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