Supplementary Information

for

Effect of Chemical Bond-type on Electron Transport in GaAs-chemical bond-Alkyl/Hg junctions

by

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Chemicals

1-dodecanethiol (>98%), 1-tetradecanethiol (>98%) and 1-octadecanethiol (>98%) were purchased from Aldrich. 1-hexadecanethiol (>95%) was purchased from Fluka. The thiols were used without further purification.

n-octylphosphonic acid (>98%), n-decylphosphonic acid (>98%), n-dodecylphosphonic acid (>99%), n-tetradecylphosphonic acid (>97%), n-hexadecylphosphonic acid (>98%), n-octadecylphosphonic acid (>97%) were purchased from Poly Carbon Industries Inc. All the chemicals were used without further purification.

Deionized water was used (18 M_).

Extra pure Hg was used 99.99999% (Fluka).

InGa was either purchased from Sigma and used as received or prepared by heating In and Ga in 1:3 (In:Ga) ratio until the mixture melted and then allowed to cool to create the eutectic mixture.

GaAs

GaAs is a III-V compound semiconductor with a cubic diamond structure (zincblende). It has a direct band gap of 1.42eV at room temperature.

(100) wafers, n-doped (Si) at 1.2-1.3 $\_10^{18}$ cm^{-3} and p-doped (Zn) at 2.5-2.6 $\_10^{18}$ cm^{-3} were purchased from AXT (CA, USA).

For the FTIR measurements undoped GaAs was used because the reflectivity in the IR region is inversely proportional to the conductivity.

GaAs Cleaning and Etching

The cleaning procedure for both the n and p-GaAs was:

1) 10 min sonication in iso-propanol (AR).
2) 10 min sonication in acetone (AR).
3) 10 min sonication in methanol (AR).
4) Drying in stream of dry N_2.
5) Ozone oxidation for 25 min in a UVOCS apparatus.

The etching procedure for both the n and p-GaAs and both for the thiols and the phosponates was:

1) 5 sec dip in 2% (by vol.) HF in DI water.
2) 3 sec dip in DI water.
3) 30 sec dip in diluted NH_4OH (1:9) in DI water.
4) Rinsed by DI water.
5) Drying in a stream of dry N_2.

Sample Preparation

After drying in a stream of dry N_2, the sample was immediately placed in the adsorption solution.

The adsorption solution for all the thiols and the phosphonates was a 5mM solution of the adsorbed molecule in the appropriate solvent.

For the thiols methanol was used as a solvent and for the phosponate we used as a solvent THF.

I-V Measurement Setup

A Hg drop was prepared with a commercial Hanging Mercury Drop (HMD) electrode apparatus (BAS, IN, USA). This system allows control over the Hg electrode, which is extruded as a drop from a column of Hg, allowing fresh drops to be produced as needed. The Hg used was 99.99999% pure. A typical drop diameter was 2 mm.

The samples were mounted on a home-built stage that allowed both coarse and fine movement of the substrate towards the Hg drop. Ohmic contacts were made to the back side of the wafers by mechanically rubbing liquid InGa onto the surface. The complete set-up was placed on a vibration-free optical table, in a class 10,000 clean room (20ºC, 40% relative humidity). The shape and area of contact was monitored optically.

ERRORS

Ellipsometry

The 5% error refers to a 2-3 nm thickness, i.e., a precision of about 0.1 – 0.15 nm, a precision, which is well reproducible (over 50 samples where measured). This does NOT represent an accuracy of 0.15 nm. The absolute scale comes, as earlier reported in ref. 2f, from combining these and the XPS data. Here we stress the differences between the thiol and phosphonate-terminated samples, and our measurement precision allows us to discuss differences down to 0.1 nm.

I-V Measurements

The reproducibility of the measurements for a given sample and from sample to sample was 10% for currents ≥ 10^{-6} A/cm^2, with a close to 100% error for the lowest currents (10^{-8} A/cm^2) that could be measured. The current densities were calculated using the optically determined contact areas.

Figure S1

Plots of current vs. reverse bias for n-GaAs/ molecules/Hg junctions. Note that in this bias range (which is completely dominated by thermionic emission over the Schottky barrier in the GaAs), all the PO_3 -bound samples have higher currents than the thiol (S-bound) ones. This can be understood from the difference in the Schottky barriers of the two systems (0.83-0.84 eV for phosphonates, 0.85-0.89 eV for thiols). This difference causes the exponential factor in the thermionic emission model to be ~ 20 times higher for the phosphonates, while the effective mass is only 5 times smaller. While this argument is valid for the reverse bias, in the forward bias range a combination of tunneling and thermionic emission already plays a role from the lowest bias values (in agreement with the, very noisy, but suggestive inversion we see in this figure at very low reverse bias).

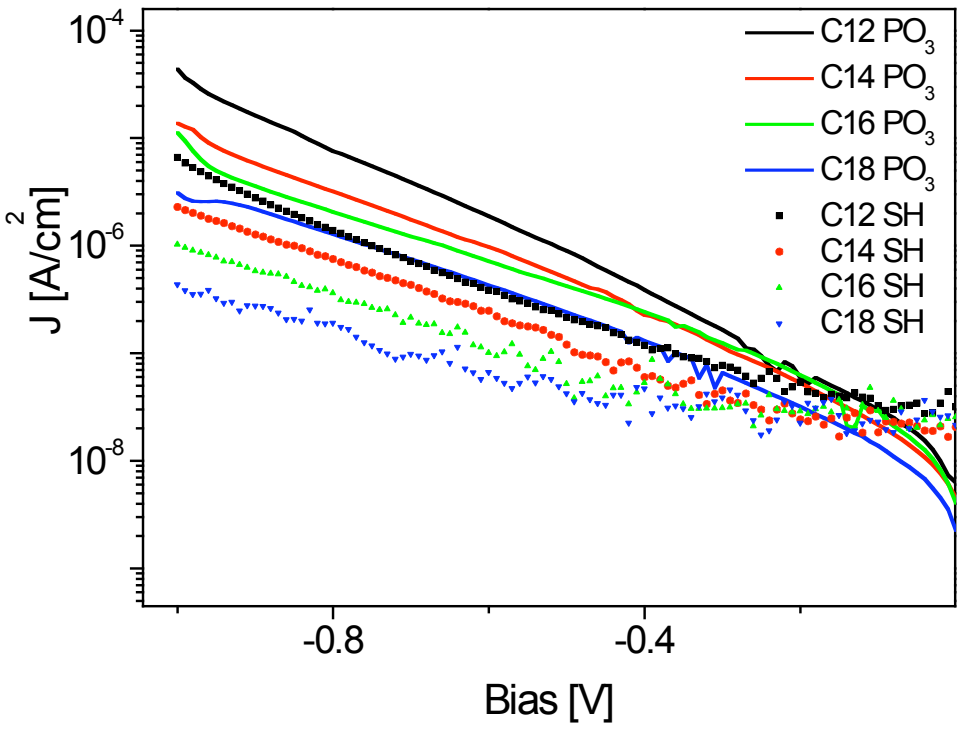

Figure S2

Plots of β^2 vs applied voltage for the p-GaAs junctions, where β is the slope of ln(*I*) vs. *d* plots, with *I* the measured current through the junction and *d* the thickness of the molecular layer as measured by ellipsometry (Table 1). Because $\_ \propto [m^*(\__t - V/2)]^{1/2}$, the plot allows extraction of the effective mass value, m*, and of the single tunnel barrier, $\__t$, that appears in the simple, linearized Simmons model. The errors for the phosphonate data are of the order of the size of the data points in the figure.

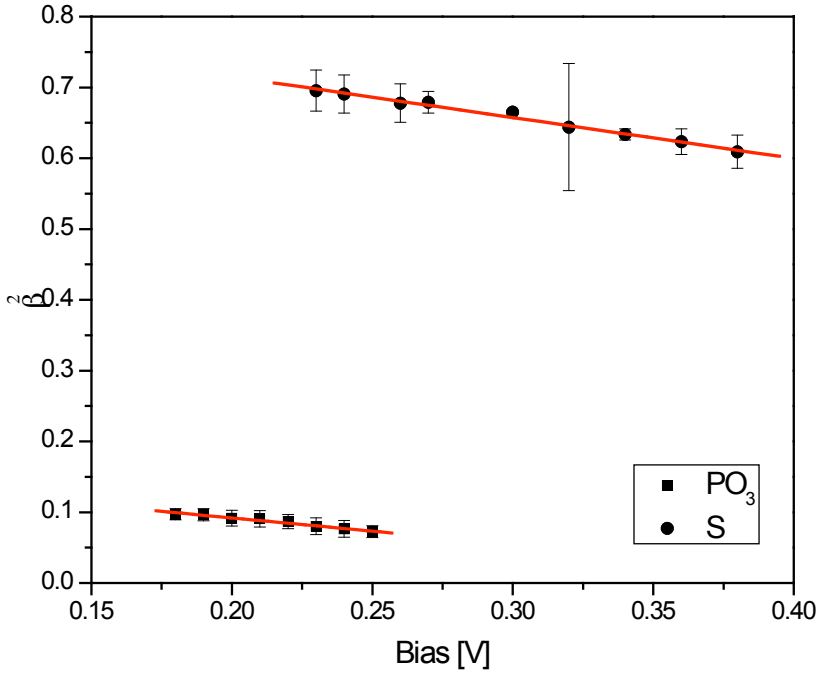

Figure S3

Plots of β^2 vs applied voltage for the n-GaAs junctions, where β is the slope of ln(*I*) vs. *d* plots, with *I* the measured current through the junction and *d* the thickness of the molecular layer as measured by ellipsometry (Table 1). Because $\_ \propto [m^*(\__t - V/2)]^{1/2}$, the plot allows extraction of the effective mass value, m*, and of the single tunnel barrier, $\__t$, that appears in the simple, linearized Simmons model. The errors for the phosphonate data are of the order of the size of the data points in the figure.