Molecular Electrodes at the Exposed Edge of Metal-Insulator-Metal Trilayer Structures

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Supplemental Material

This supplemental section is provided to display data and analysis too lengthy for archived journal space but is helpful for the reader to further judge the validity of the data. In particular curve fits and analysis is shown for the fit of Simmons tunnel model to observed experimental data. Also temperature dependence and alkane bridged transport is shown.

S1.1 Simmons fit uncertainty

We have modeled our molecular junction's I-V or Current density-Voltage data using Simmons model in *intermediate* voltage range (eq.1).

$$j=\left(\frac{e}{4\pi^2\hbar d^2}\right)\left\{\left(\varphi_B-\frac{eV}{2}\right)\times\exp\left[-\frac{2(2m)^{1/2}}{\hbar}\alpha\left(\varphi_B-\frac{eV}{2}\right)^{1/2}d\right]-\left(\varphi_B+\frac{eV}{2}\right)\times\exp\left[-\frac{2(2m)^{1/2}}{\hbar}\alpha\left(\varphi_B+\frac{eV}{2}\right)^{1/2}d\right]\right\}$$

(1)

where m is electron mass, d is barrier thickness, φ_B is barrier height, V is applied bias , and α is a unitless adjustable parameter, that allows for deviations from a simple rectangular barrier and effective mass of the free electron. Via equation 1, (setting α =1) we are able to fit the values of *both* barrier height and barrier thickness before and after molecule attachment. This can be a tricky curve fit since we are extracting parameters from a change in curvature. We calculated barrier height and barrier thickness assuming barrier to be of rectangular shape and electron mass to be of free electron mass. Experimental current density data used for analysis was for ~ 0-0.4V range. For bare electrodes, Simmon's fit gave expected values for tunneling through the Al_2O_3 oxide layer.

After molecule attachment, Simmon's model resulted in a reasonable fit with parameters consistent with molecule geometry. Both barrier height and barrier thickness, were fit to yield minimum difference between experimental and calculated current density (σ^2 = 1/N*Σ((Iexp-Icalc)/Icalc)^2). In order to see the variation of fitting parameters the following table and plot are shown of Simmon's fits to experimental current. The first table entry is the best fit (highlighted green) of both barrier height and thickness. The next two sets show the variation of curve fit by setting barrier thickness (or height) and fitting barrier height (or thickness) near the best fit. This shows that the fitting uncertainty is ~0.1eV for barrier height and ~1 angstrom for thickness. The error bars in Figure 9 (manuscript) due to sample to sample variation are significantly larger (0.3eV and 2 ang) than uncertainty of the fit.

Best Fit result (both barrier height and width fit to exp. data)

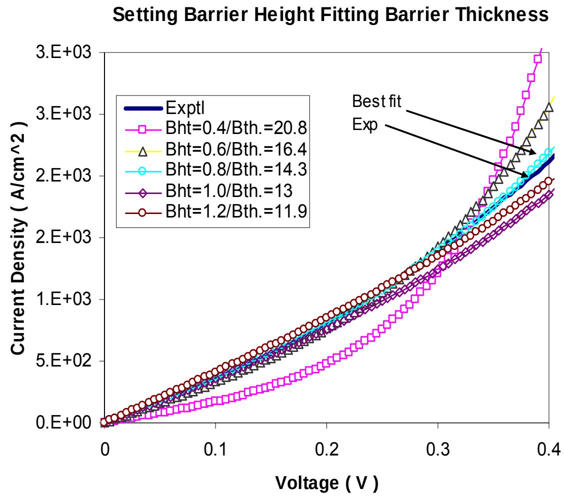
Barrier Thickness(?)	Barrier Height (eV)	σ^2
14.3	**0.8**	**0.01317**

Set Barrier thickness **Fit barrier height**

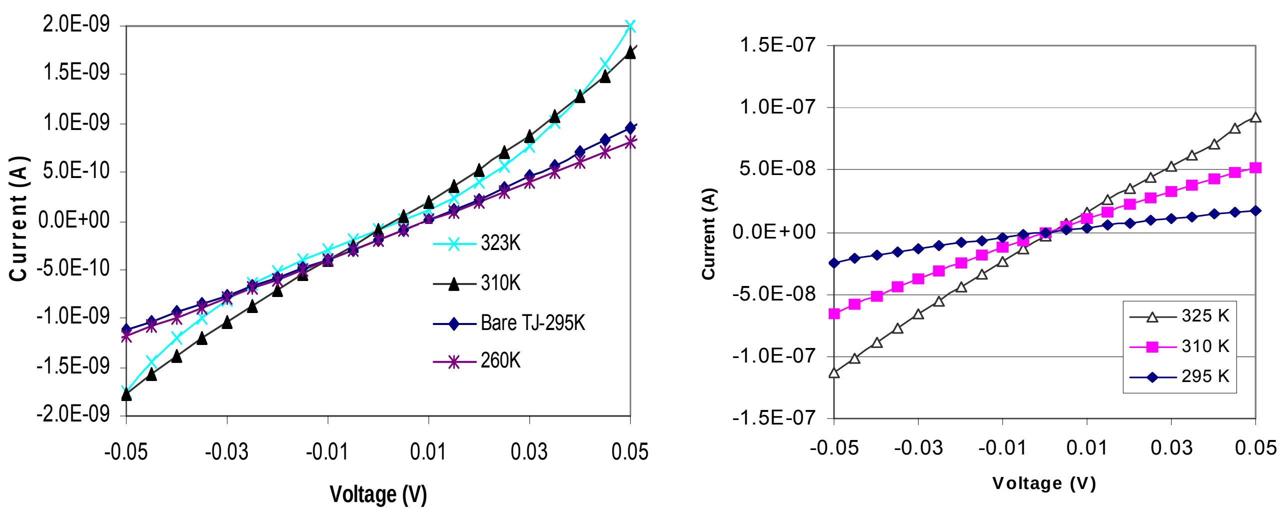
Barrier Thickness(?)	Barrier Height (eV)	σ^2
10.3	1.7	0.049321
11.3	1.4	0.036657
12.3	1.1	0.031224
13.3	1	0.018248
14.3	**0.8**	**0.013171**
15.3	0.7	0.014936
16.3	0.6	0.036634
17.3	0.6	0.260559
18.3	0.5	0.08649
20.3	0.4	0.331173

Set Barrier height **Fit barrier thickness**

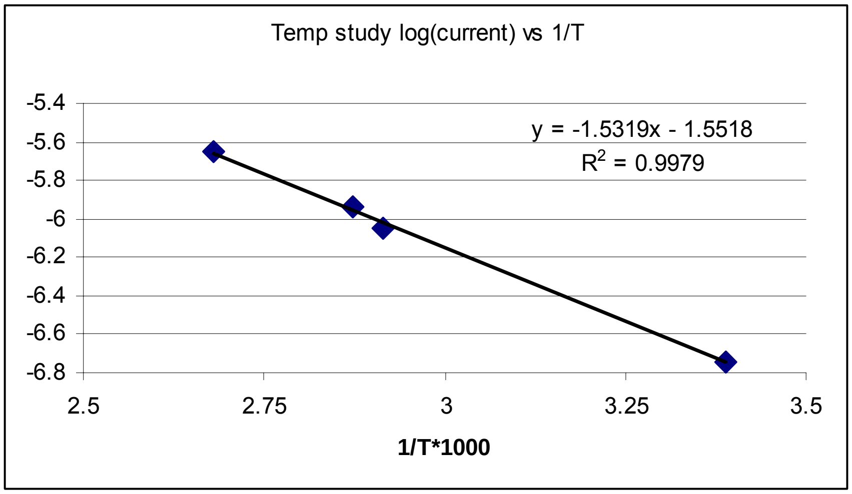
Barrier Thickness(?)	Barrier Height (eV)	σ^2
0.4	20.8	0.235344
0.6	16.4	0.024716
0.8	**14.3**	**0.013171**
1	13	0.018248
1.2	11.9	0.023075



S1.2 Temperature dependent transport through Ta/AlOx/Ta based MEME

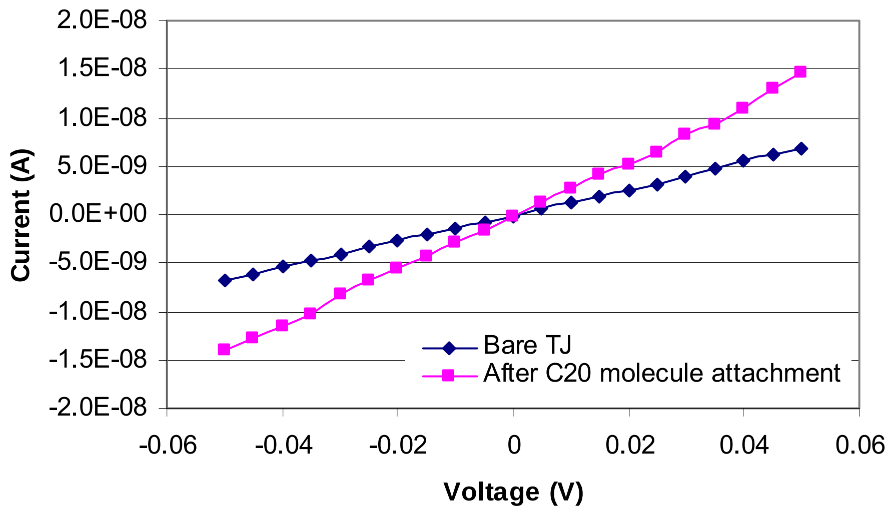


Effect of temperature on transport through bare Ta/AlOx/Ta tunnel junction [Right] and after molecule attachment [Left].



T (K)	Current (A) at 50mV	activation energy (eV)
295	1.82E-07	
343	8.94755E-07	0.29
348	1.16108E-06	0.31
373	2.22664E-06	0.3

S1.3 Transport through C20 bridged MEME



Dithiol-alkane with 20 carbon atoms nominally enhances the tunnel junction current across electrode due to long tunnel length compared to metal cluster with shorter tethers to metal center.