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Interfacial Transport Properties in Metal-Molecule-Semiconductor Diodes

Julia W. P. Hsu

Sandia National Laboratories

W. Li, K. Kavanagh (*Simon Fraser)*

Y. Jun, X. Y. Zhu *(Univ. of Minn.),* D. A. Krapchetov, D. A. Fischer, Y. L. Loo (*UT-Austin*), C. Highstrete, C. M. Matzke, M. Clift, A. A. Talin, F. Leonard, S. Faleev (*Sandia),*

M. D. Halls, K. Raghavachari (*Indiana Univ)*

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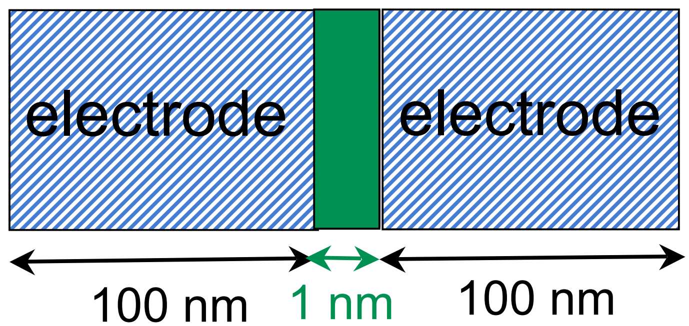
Background

- Molecular electronics are targeted for applications in computing, memory, & sensing
- These applications require passing current through the molecules/molecular layers, hence making electrical contacts

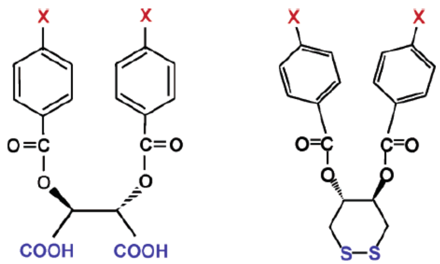


1. The deposition of the top contact could change the monolayer, induce dipole, change band alignment, etc
2. The active molecules are sandwiched between 2 electrodes and not easily accessible

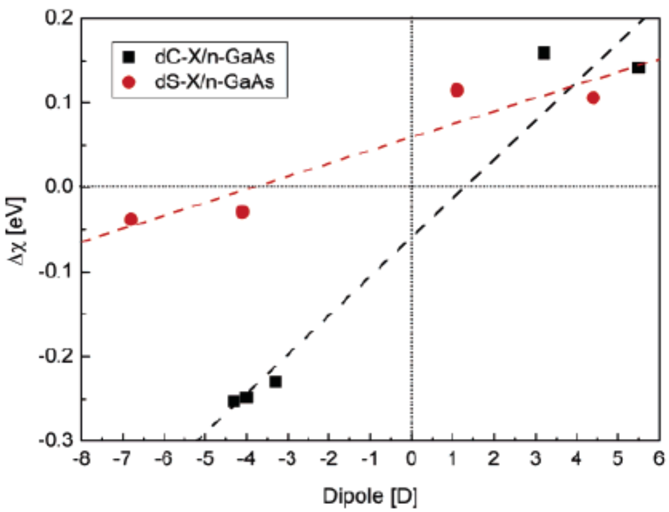
Motivation

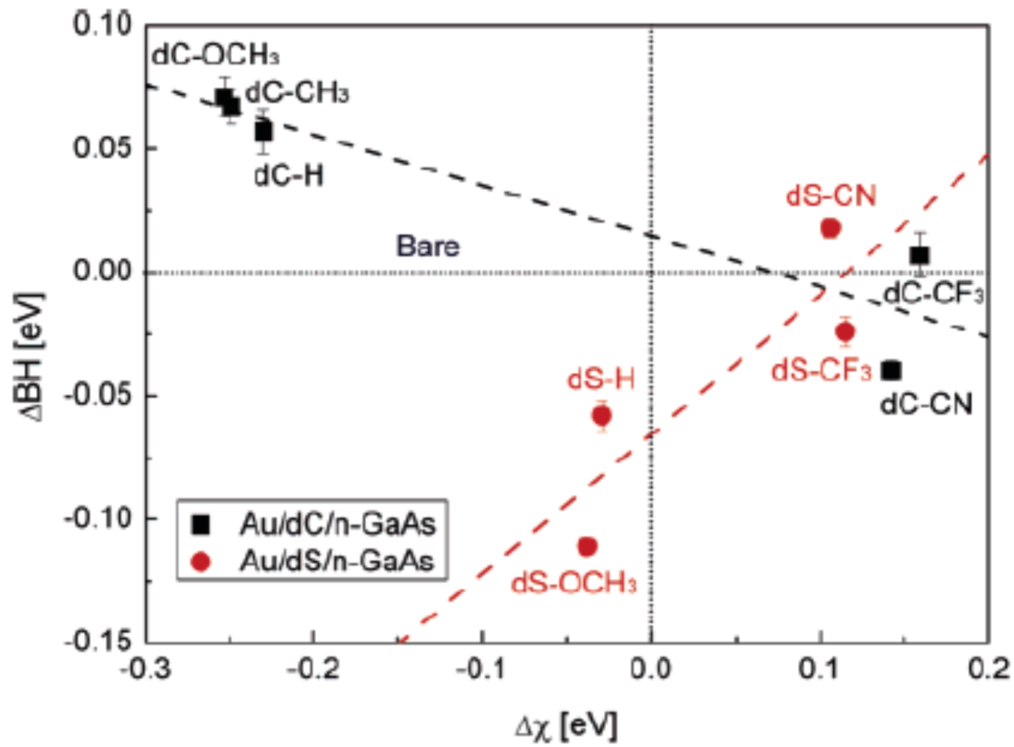
Change in monolayer

Haick, JPCB 109, 9622 (2005)



dC dS





- Hence, there is a need to probe electrical transport across the buried interface in finished devices
- Few techniques are available

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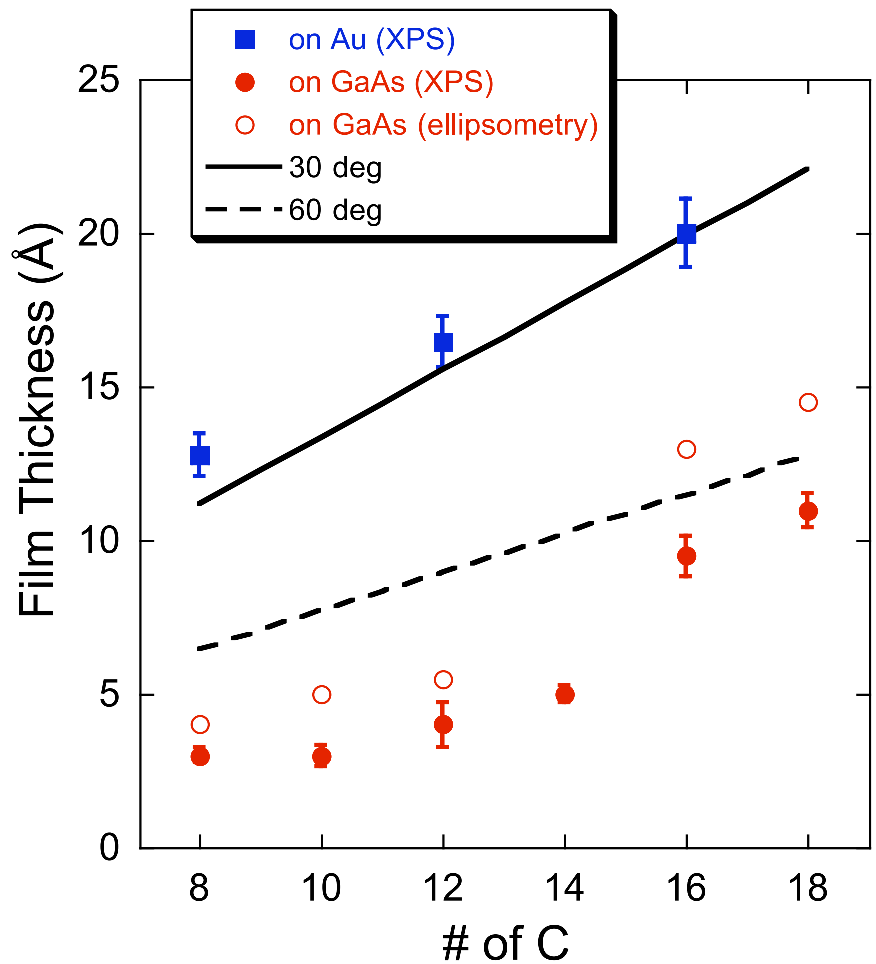
Outline

- Formation of Thiol and Dithiol Monolayers on GaAs (001)
  - Model system for molecular-semiconductor hybrid electronics
- I-V-T Measurements of Molecular Diodes
- Ballistic Electron Emission Microscopy (BEEM)
- BEEM Images & Spectra
  - Control (Au/GaAs)
  - Hexadecanethiol (Au/C16MT/GaAs)
  - Octanedithiol (Au/C8DT/GaAs)
- Interpretation of BEEM results
- Difference between C8DT and C16MT

Langmuir 22, 3627 (06)

Thiol formation on GaAs

- XPS (attenuation of Ga_{3d}), ellipsometry
- Previous works limited to C18MT
- Short molecular length thiols (n ≤ 14) do not form good monolayer: small C signal, tendency to form oxides
- Long molecular length (n ≥ 16) consistent with 60° angle



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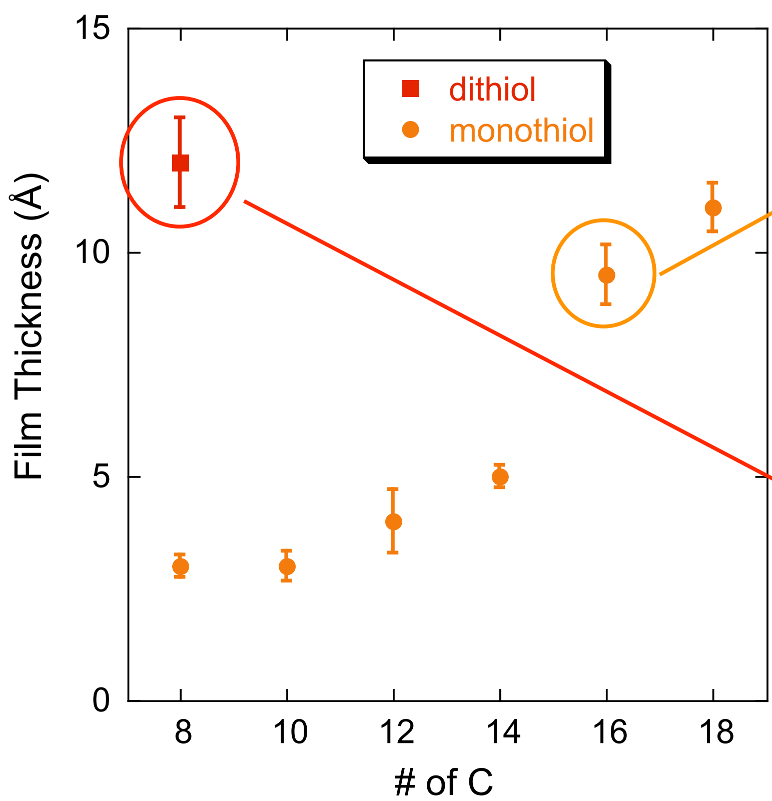
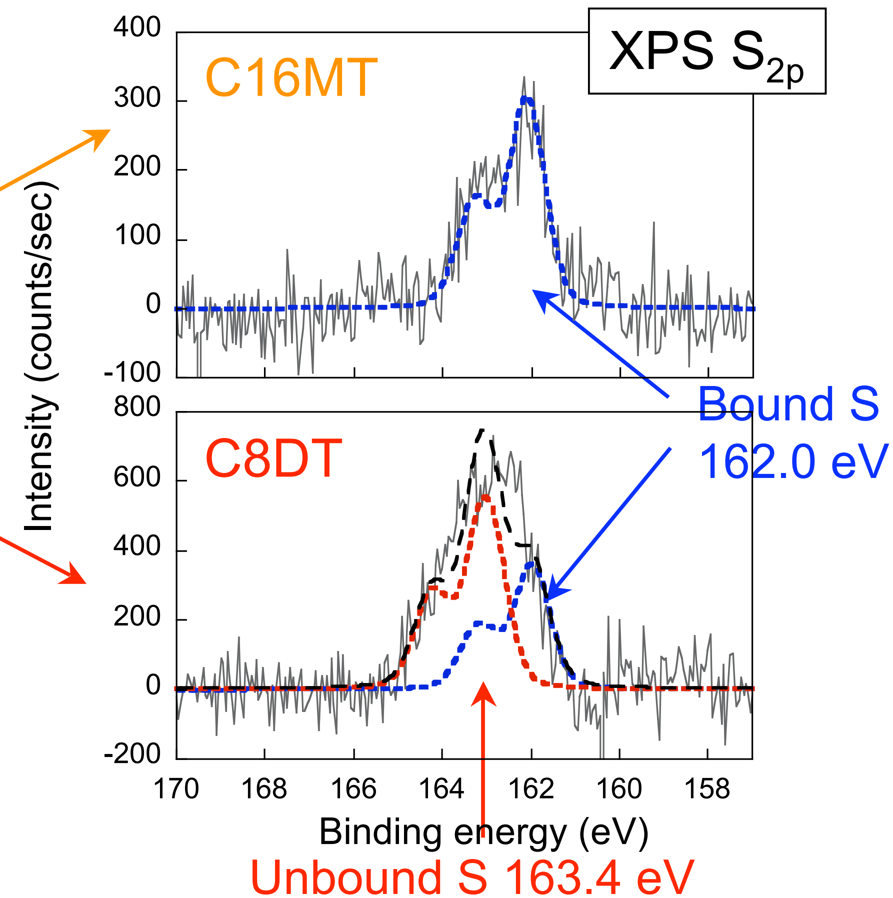
C8DT Formation on GaAs





- C8DT is 12 Å thick: a dense monolayer w/ orientation almost normal to surface!

- C8DT: B:UB = 1 : 1.45; consistent with 11 Å film
- No S-O or S-S

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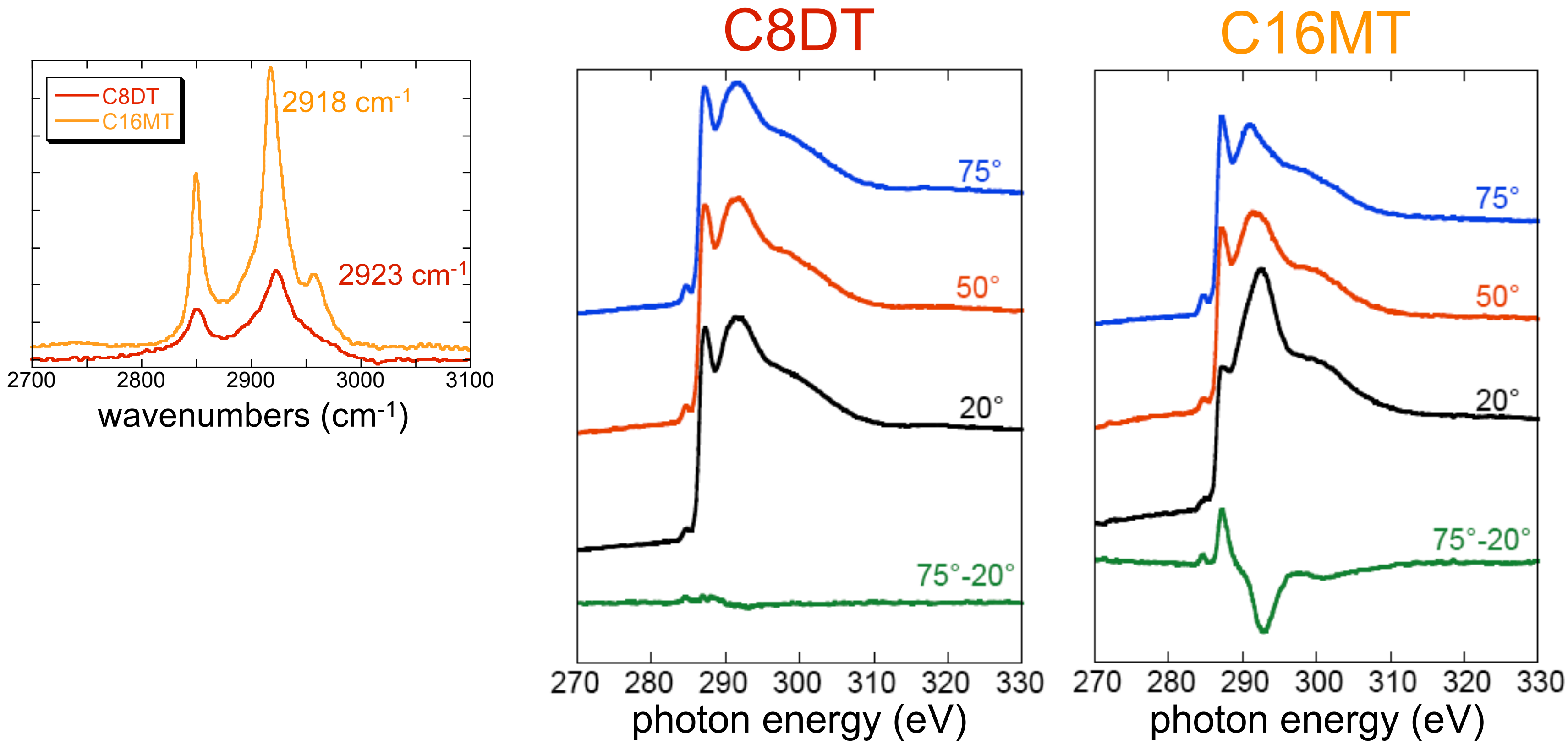
FTIR & NEXAF Results



- C8DT does not show in-plane orders.
- C16MT exhibit in-plane order with ~ 35° tilt on average.
- How to reconcile with XPS and ellipsometry results?

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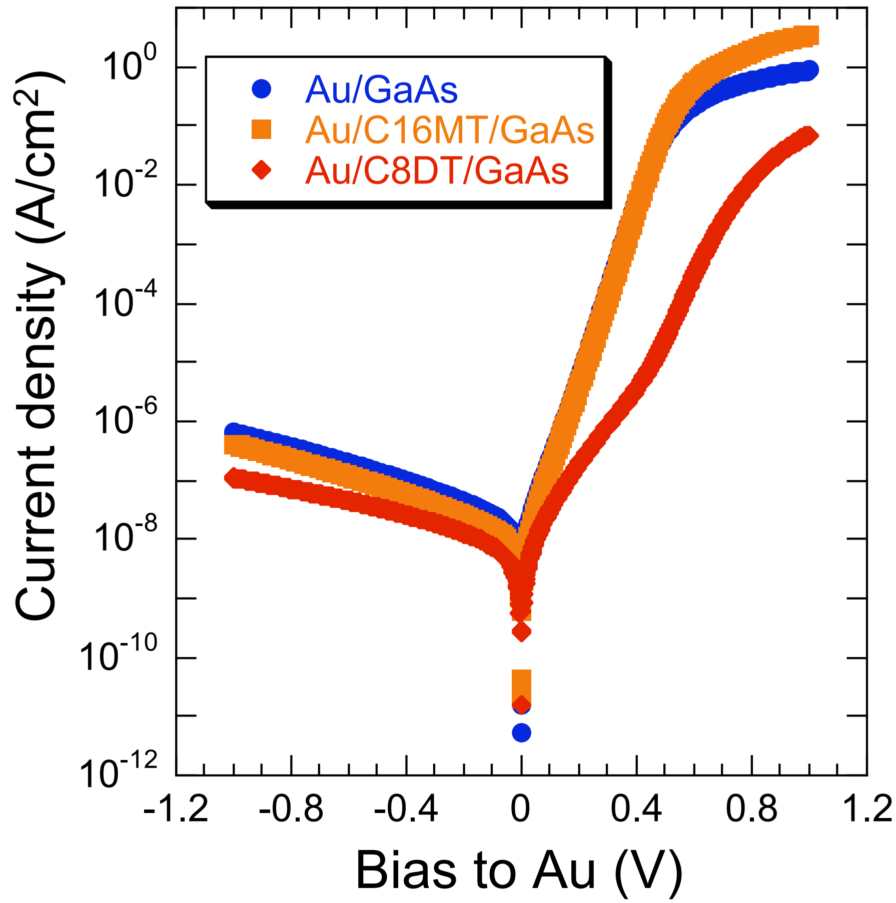
Room Temp I-V

- Au-molecule-GaAs diodes (125µm - 1mm diameter), where molecule = C8DT & C16MT
- Control: Au/GaAs
- n-GaAs (Si doped: 2E17 cm^{-3})
- Top Au contacts made by e-beam evaporation (direct, 10 Å/s)
- No significant difference in Schottky barrier heights, but n increases



$$J = A^{**}T^2 \exp\left(-\frac{q\phi_{bn}}{kT}\right)\left[\exp\frac{qV}{nkT} - 1\right]$$

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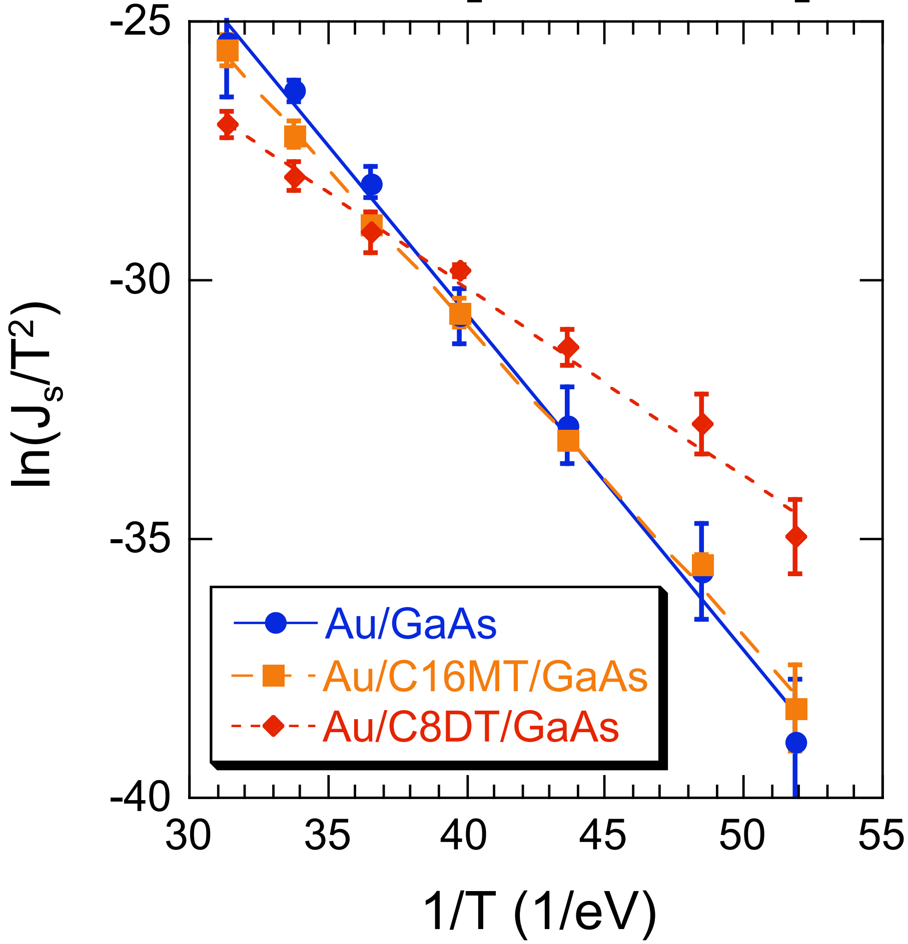
Temperature Dependence

$$J = J_s\left[\exp\frac{qV}{nkT} - 1\right]; J_s = A^{**}T^2\exp\left(-\frac{q\phi_{bn}}{kT}\right)$$



- C16MT diodes are similar to control; C8DT diodes are different
- ϕ_{bn} obtained from I-V-T are substantially smaller than RT values (0.65, 0.6, 0.36 eV)
- A^{**} are small compared to theoretical value (10^{-2}, 10^{-3}, 2×10^{-7} A/cm^2/K^2)

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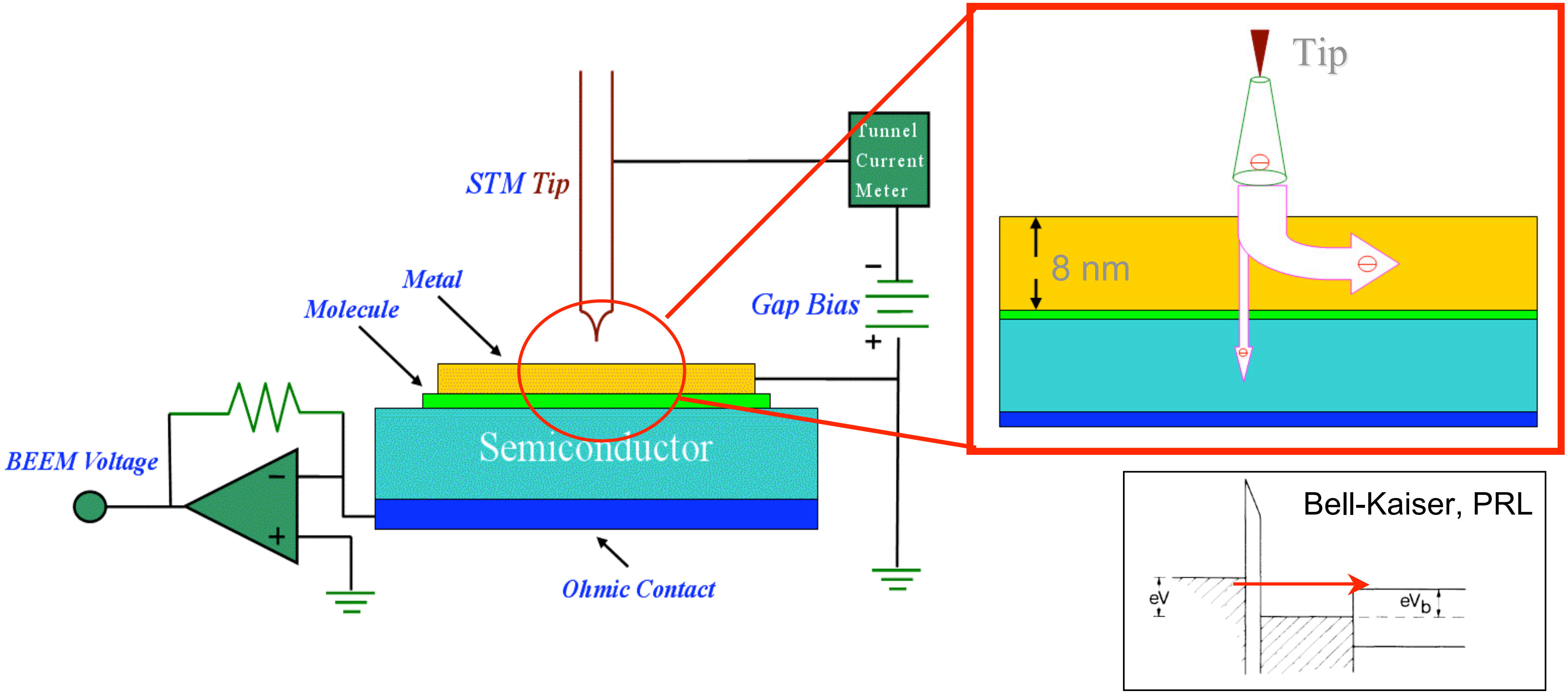
Ballistic Electron Emission Microscopy



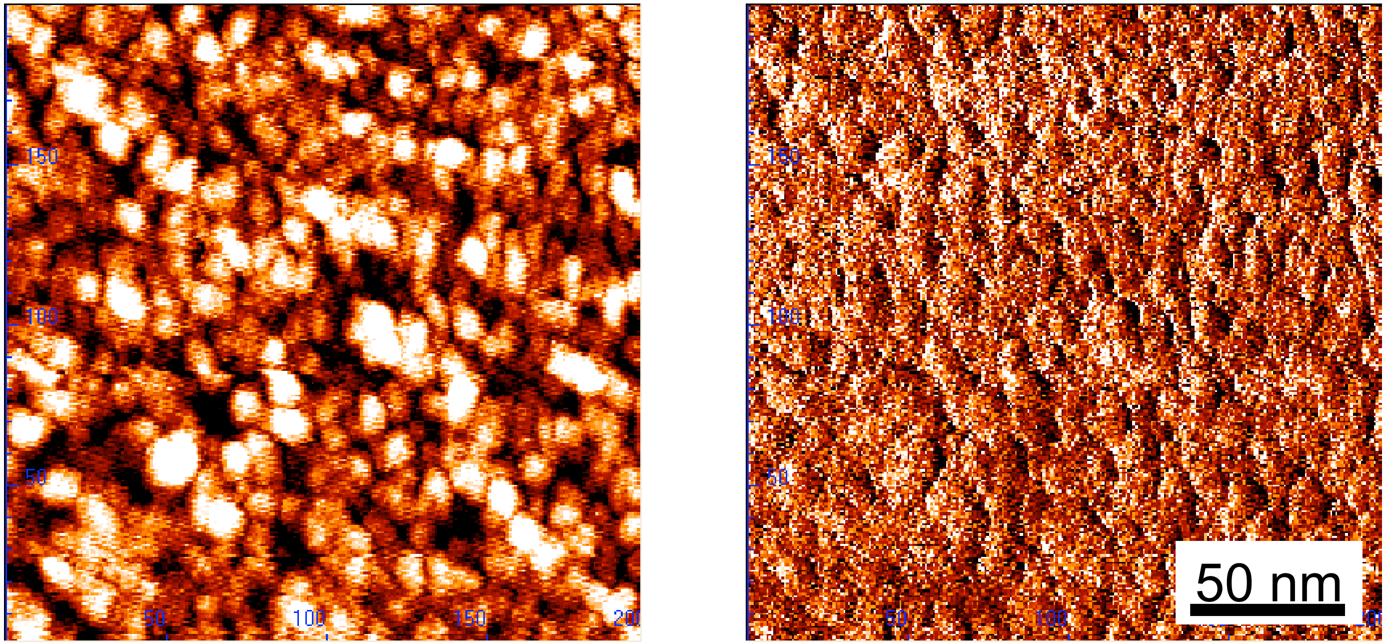
- Spatially resolved (10-20 nm) measurement
- No applied bias (< 10 mV) across the molecules
- BK model $I_c = R I_t C (V - V_b)^2$ I_t ~ nA; I_c ~ pA

Control (Au/GaAs)

STM (topography)

V_t = -2.1V, I_t = 20 nA

BEEM

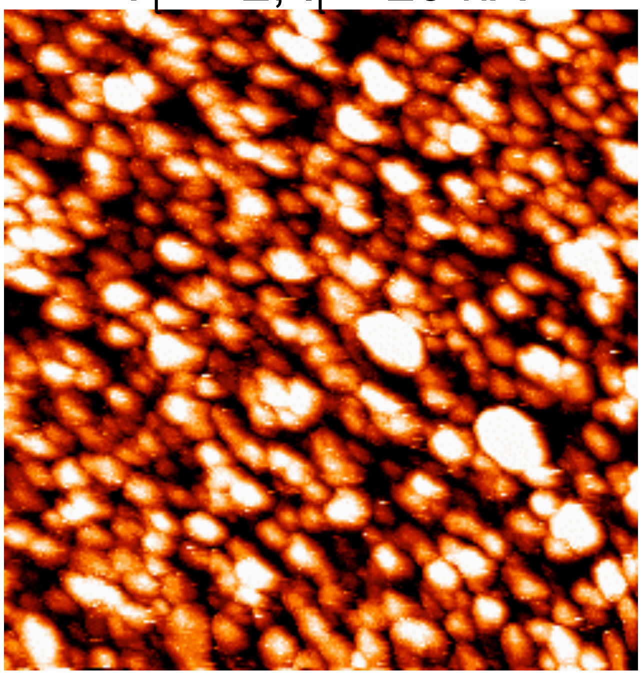


- More or less uniform BEEM signal with some grain to grain variations
- Threshold 0.87 V, consistent with other Au/GaAs BEEM results

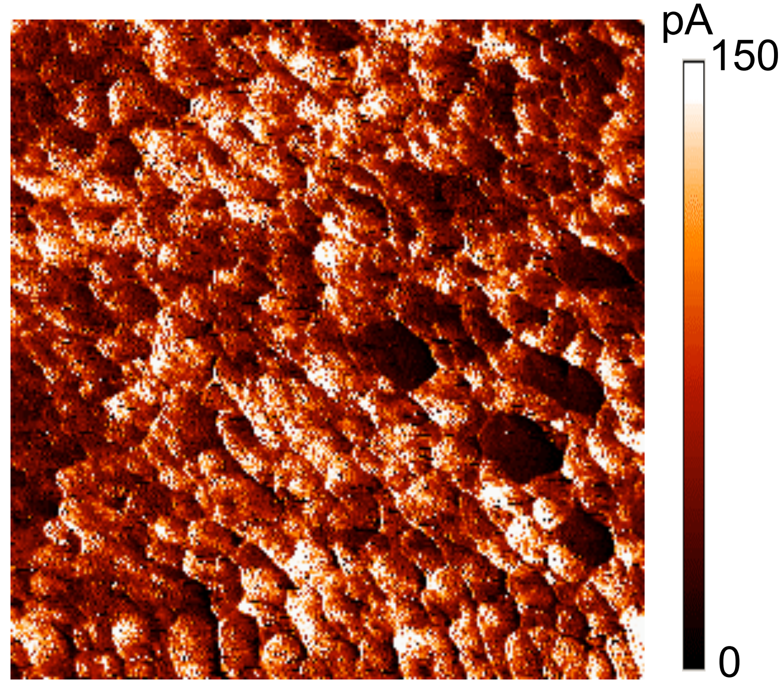
Au/C16MT/n-GaAs

STM (topography)

V_t = -2, I_t = 20 nA



BEEM

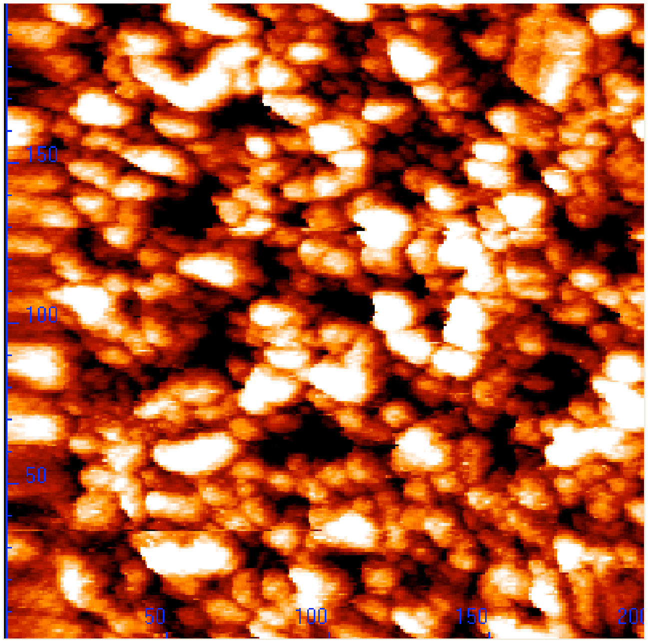


- Uniform BEEM signal, similar to Au/GaAs
- Threshold is 1.1V, not 0.87V of Au/GaAs

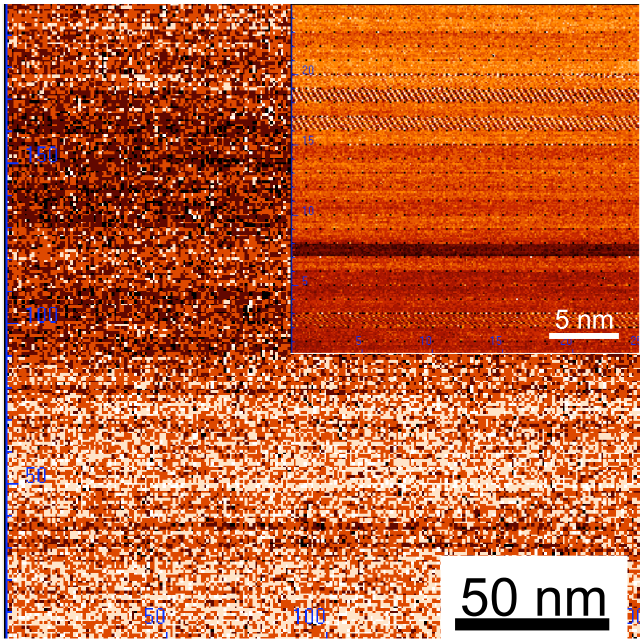
Au/C8DT/GaAs

STM (topography)

V_t = -1.0V, I_t = 20 nA



BEEM



- Most areas have no BEEM signal at all
- Whenever there is a BEEM signal, the threshold is 1.5V, not 0.87V of Au/GaAs, nor 1.1V of C16MT

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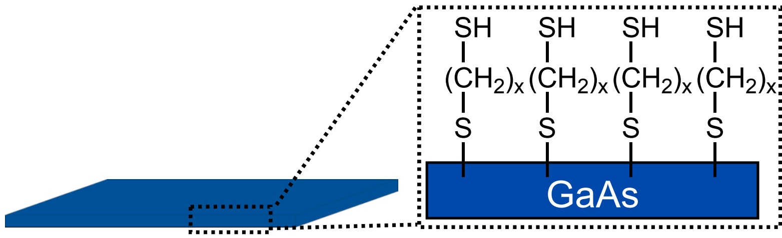
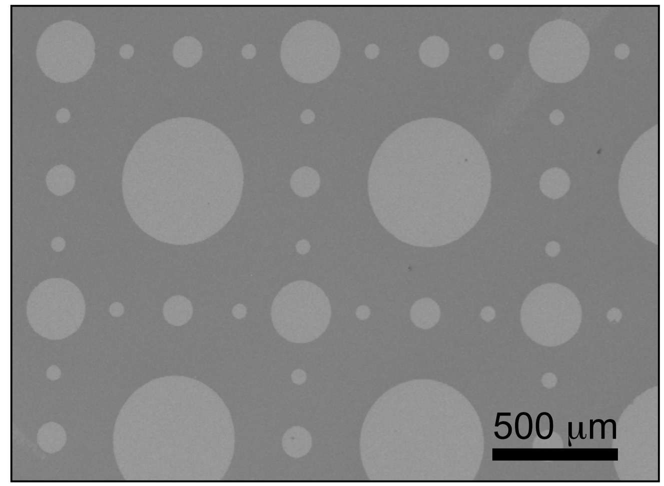
Nanotransfer Printing (nTP)

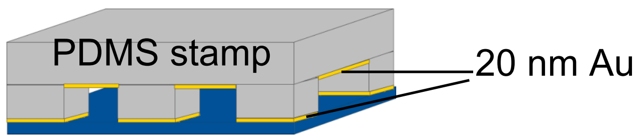
Loo, JVST B**20**, 2853 (2002)

(a) Etch oxide; deposit dithiol layer

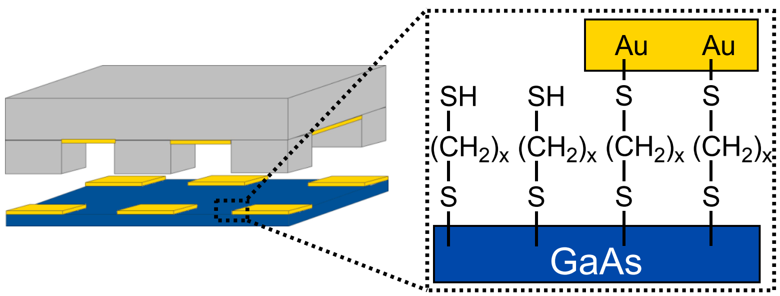


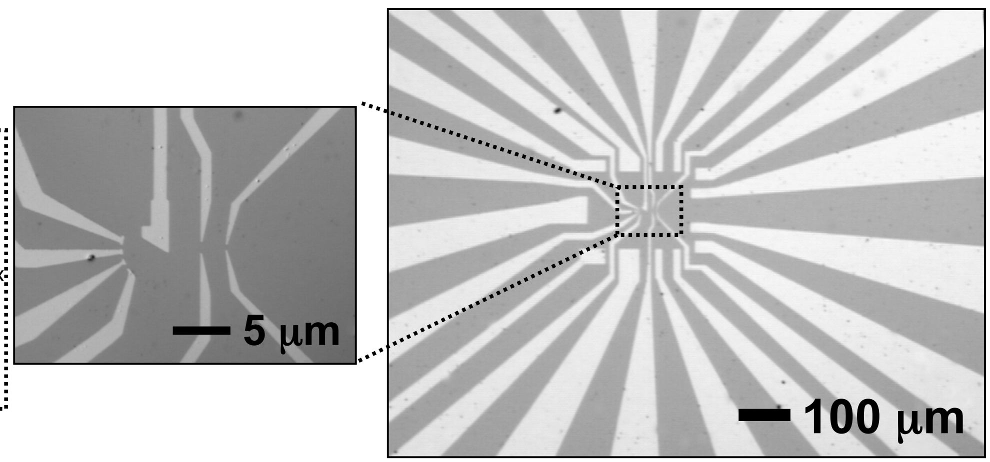


(b) Bring stamp into contact with substrate



(c) Remove stamp; complete nTP



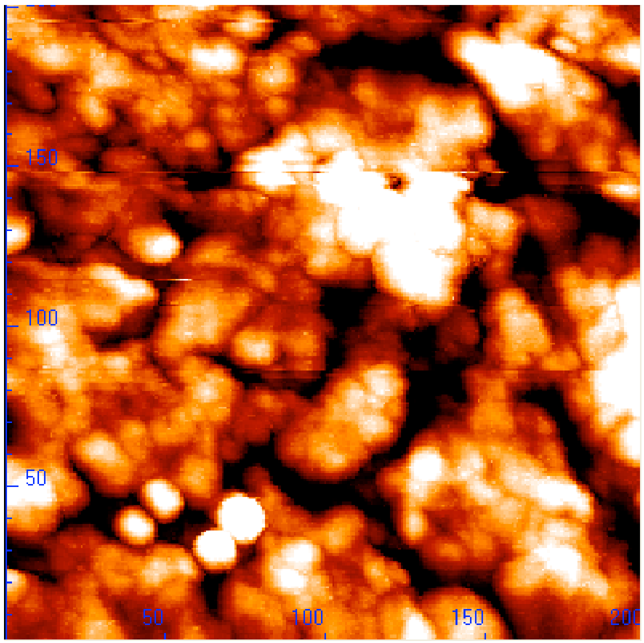


Pass Scotch tape test!!! ⟹ Chemical bonding

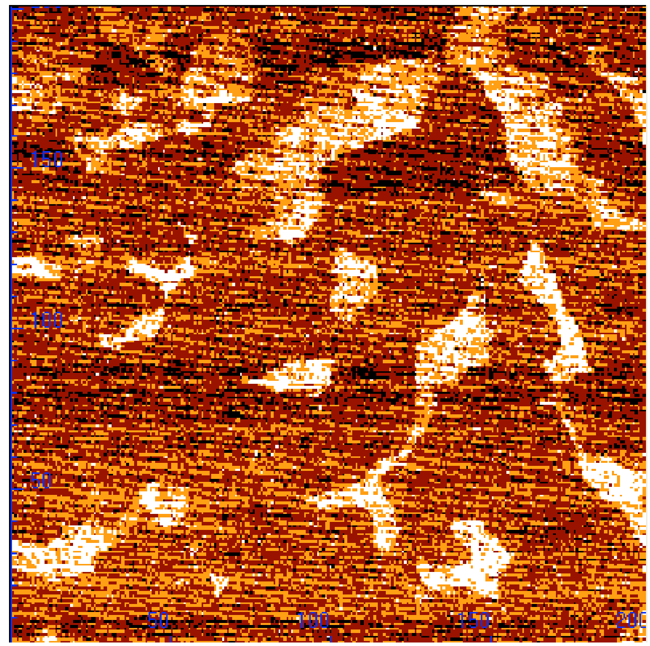
nTP (Au/C8DT/GaAs)

STM (topography)

V_t = -1.8V, I_t = 20 nA

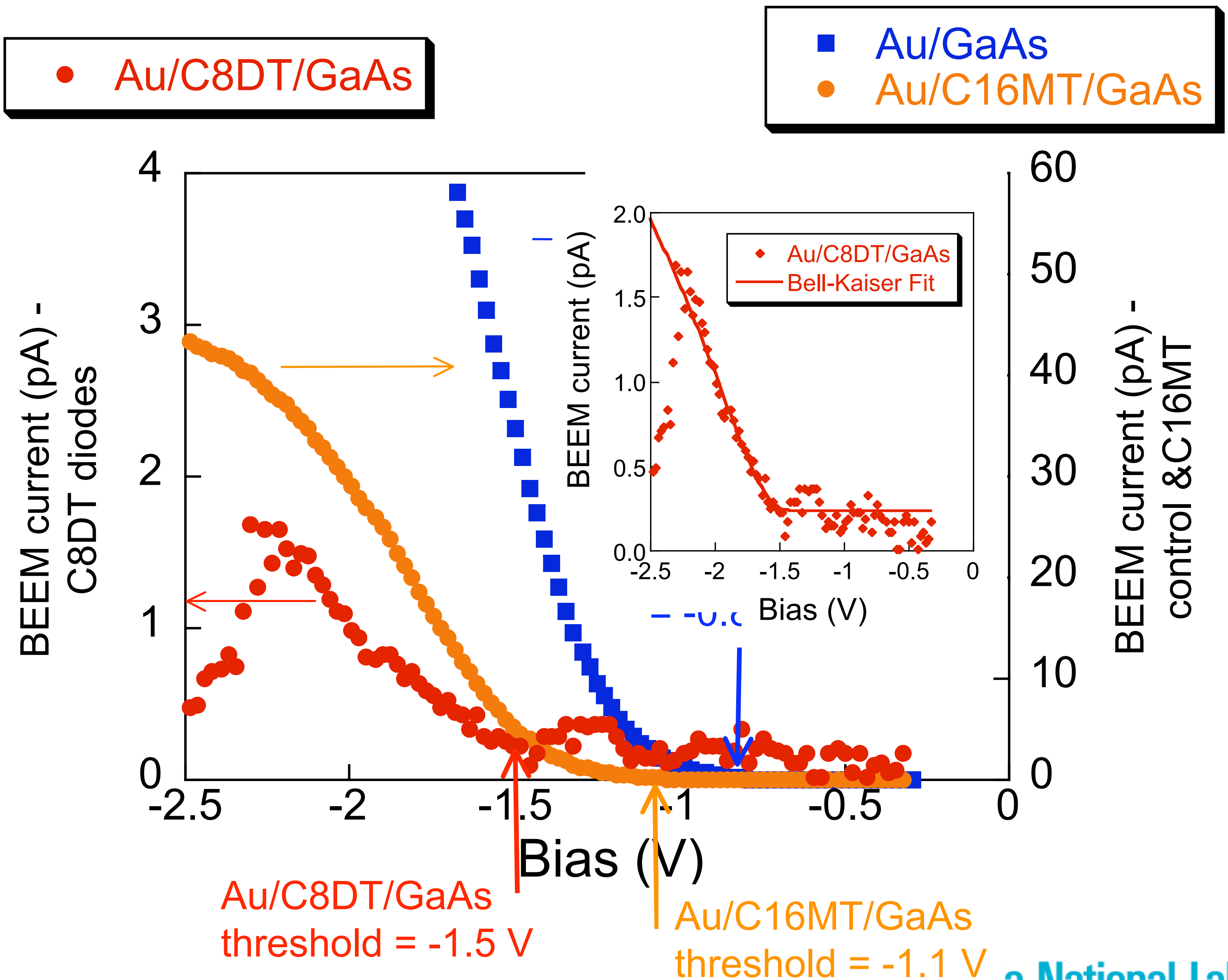


BEEM



- Some regions do show BEEM signals in patches
- Larger BEEM signal in depressions
- Threshold 1.45 V
- BEEM signals disappear after 3 scans

BEEM Spectra



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Summary of Experimental Results

Very consistent

	RT I-V Barrier (V)	BEEM Threshold (V)	BEEM Image	BEEM Spectra
Control	0.71-0.83 n=1.47-1.12	0.86	uniform	monotonic
C16MT	0.74-0.80 n=1.89-1.37	1.1 } ?	uniform	monotonic
C8DT	0.74-0.84 n=2.52-1.49	1.5 }	Spotty (agree with low A**)	I drops above ~2V

Sample (GaAs) Dependent

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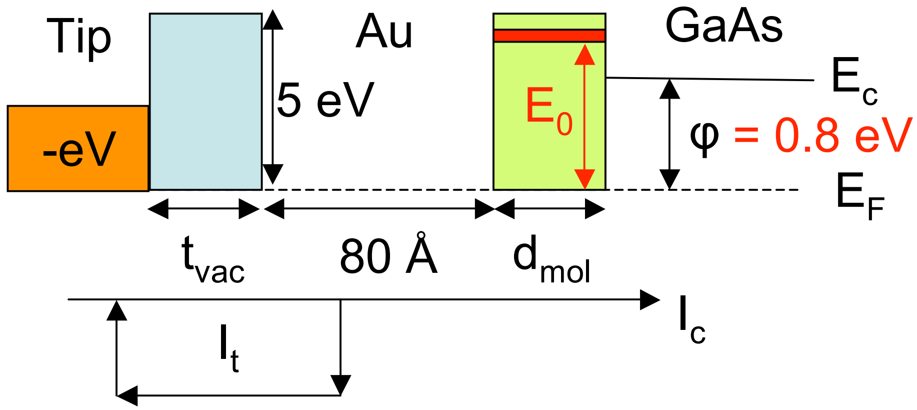
JPCB **109**, 6252 (2005)

Double-barrier Model



Approach: Solve Schrodinger's equation analytically in 1D, calculate transmission probability T(E), tunneling current (I_t) and BEEM current (I_c).

$$I_t(V) = \int T_{vac}(E)\left[F_{tip}(E - eV) - F_{Au}(E)\right]dE$$

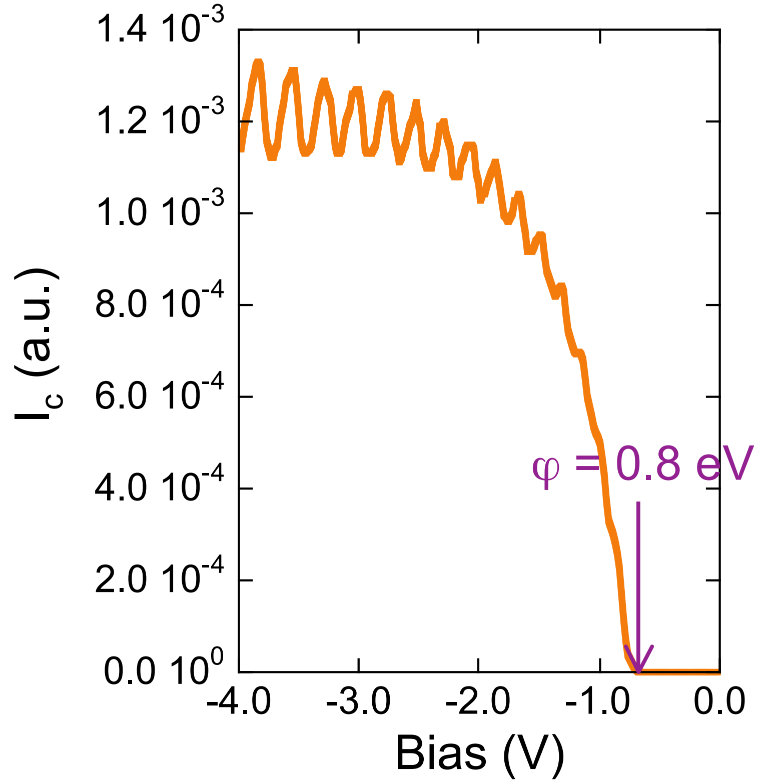
$$I_c(V) = \int T_{tot}(E)\left[F_{tip}(E - eV) - F_{GaAs}(E)\right]dE$$

$$T_{tot}(E) = \begin{cases} T_2(E) & |E - E_0| > 2\sigma \\ T_{vac}(E) x T_{mol}(E) & |E - E_0| < 2\sigma \end{cases}$$

$$T_{mol}(E) = f \exp\left[\frac{-(E - E_0)^2}{\sigma^2}\right]$$

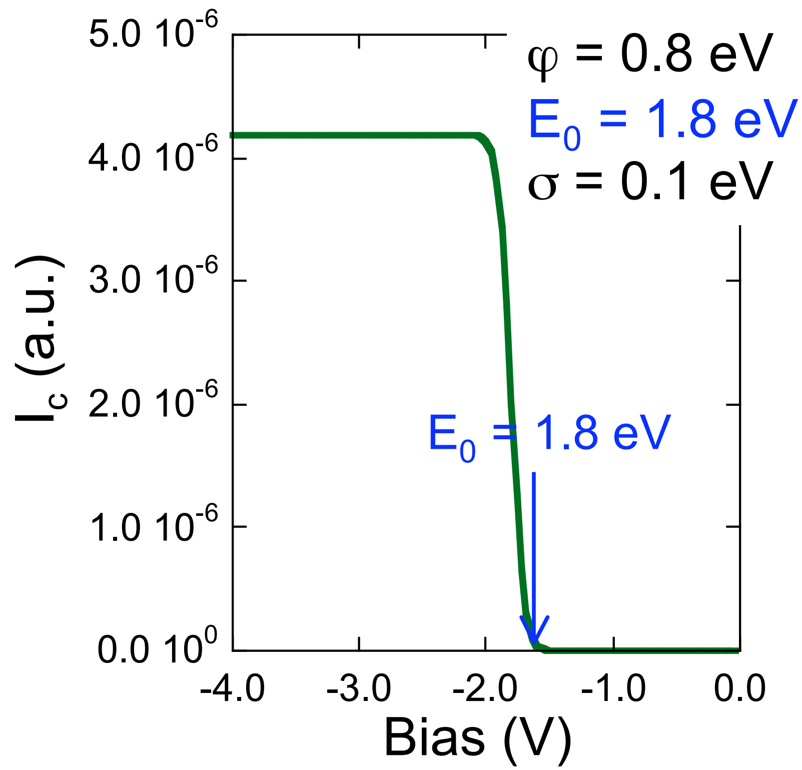
No Molecular Levels constant current

φ = 0.8 eV; t_{mol} = 5Å



- BEEM threshold determined by φ
- I_c saturates but does not decrease
- Oscillation due to thin Au

With Molecular Levels but constant height



- BEEM threshold determined by E_0
- I_c saturates but does not decrease
- If the level is localized, the same behavior with lower I_c (smaller f).

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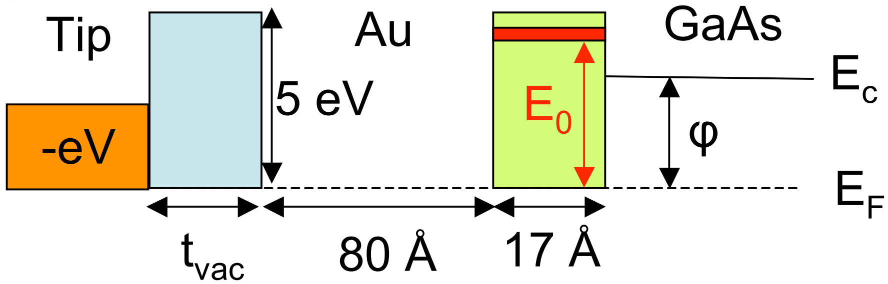
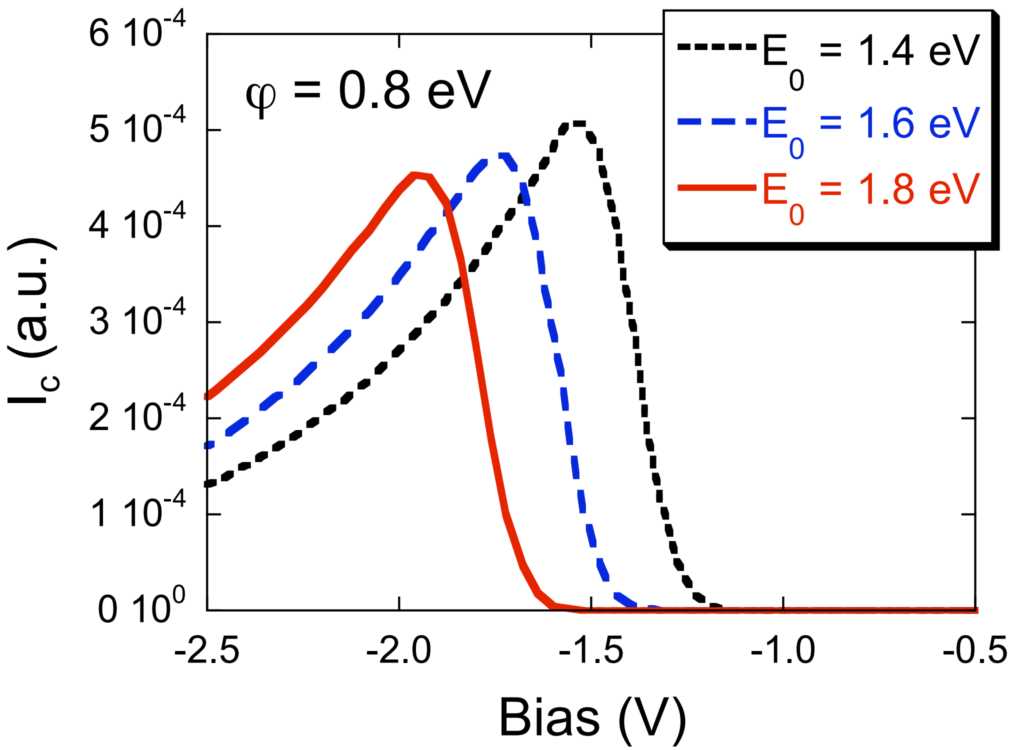
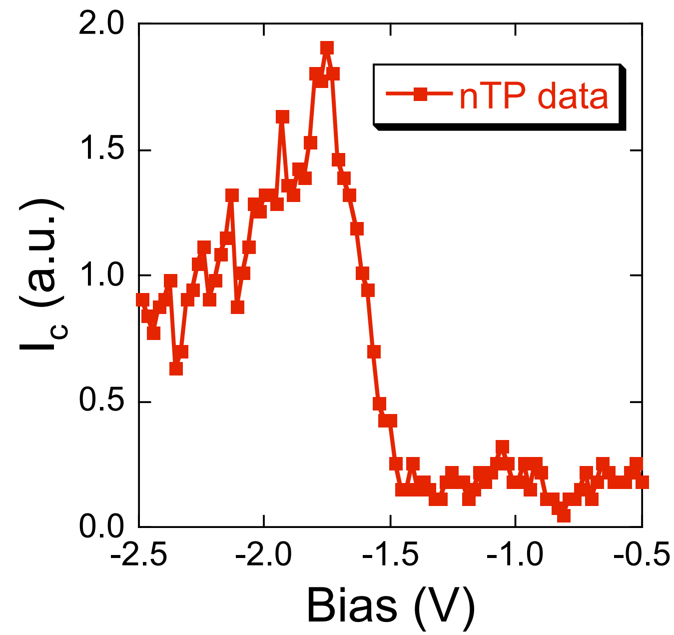
With Molecular Level (constant current)



- BEEM probes lowest unoccupied states
- I_c decreases due to constant current feedback and finite width of the molecular level





JPCB **109**, 6252 (2005)

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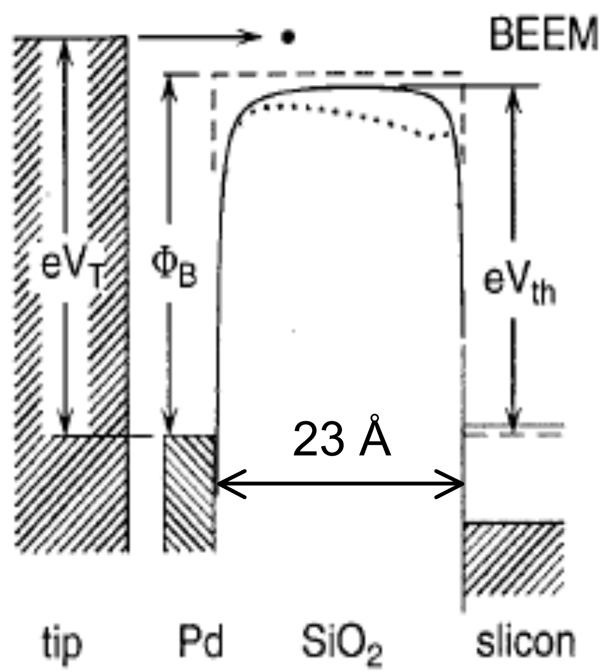
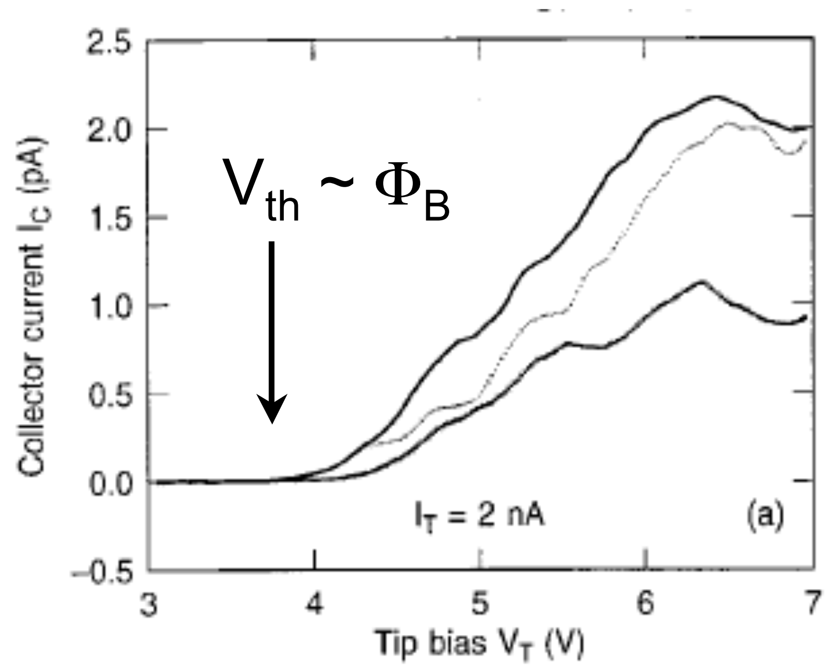
Previous MIS Results

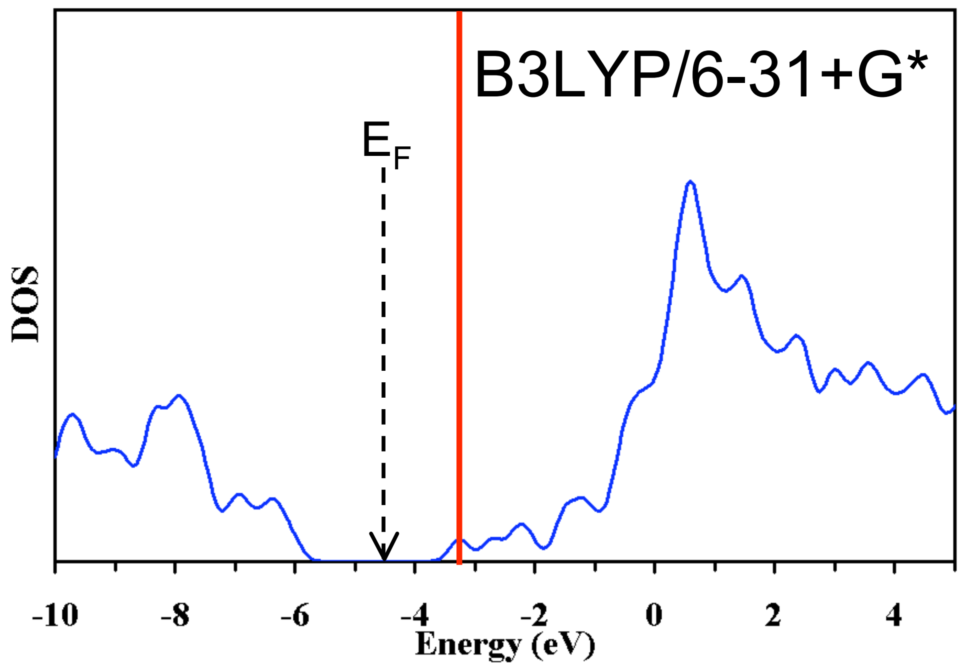
•*R. Ludeke and A. Schenk, J. Vac. Sci. Technol. B, Vol. 17, No. 4, Jul/Aug 1999*



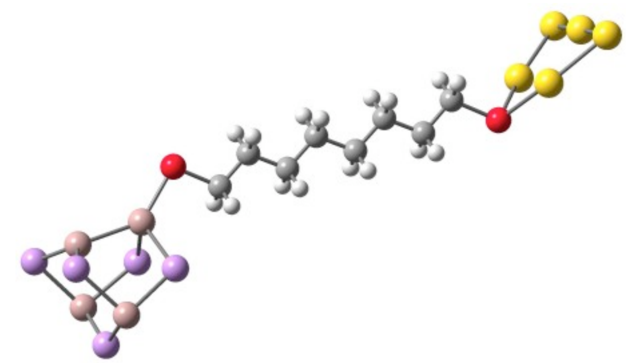


BEEM threshold determined by the energy difference between E_F of metal and conduction band of insulator

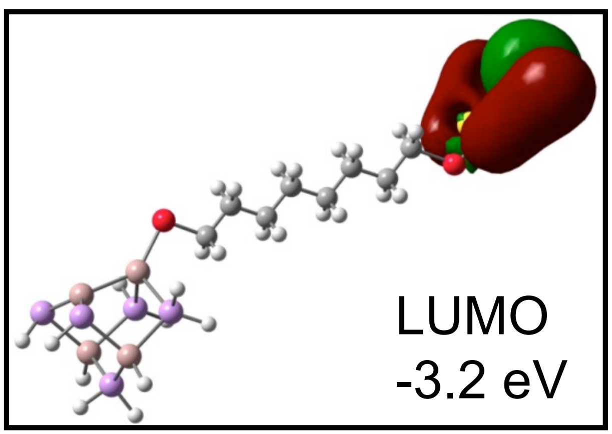
Candidate for MO at E_0:
Electronic Structure Calculation



JPCB **109**, 5719 (2005)



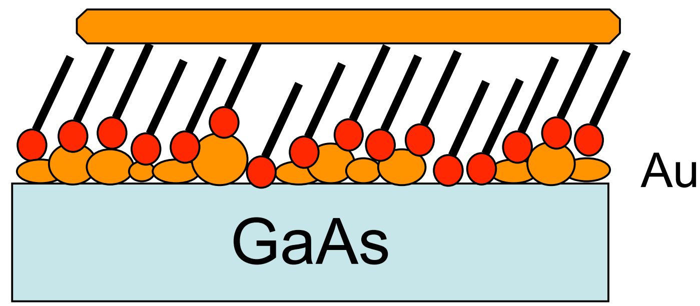
"HOMO-LUMO" gap = 3 eV



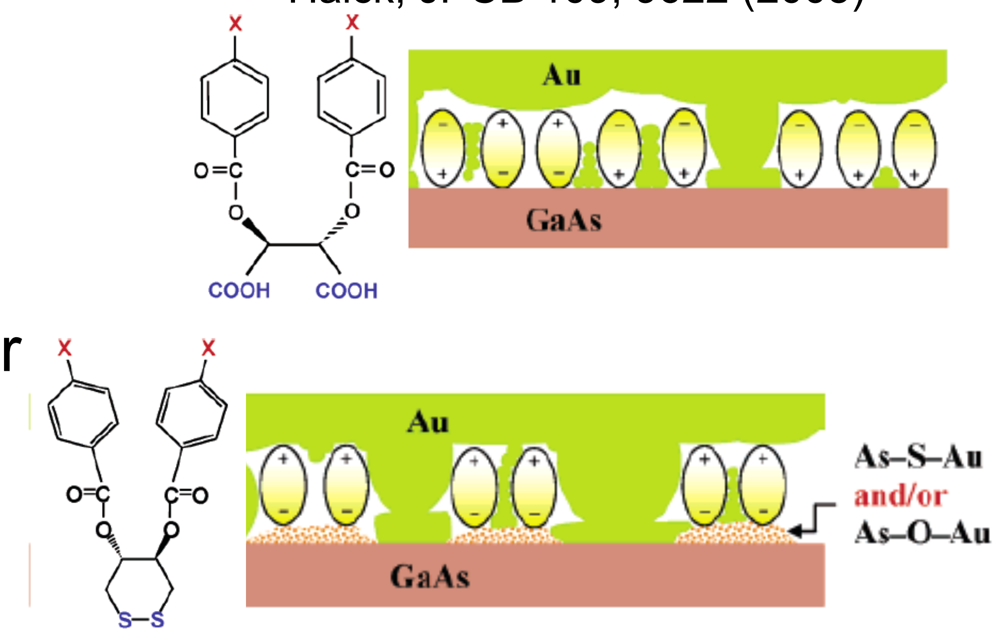
- LUMO ~ 1.5 - 2 eV above E_F
- Localized at Au interface: small f
- S bond to Ga; Exp: S bond to As?

Why are C8DT & C16MT diodes different?

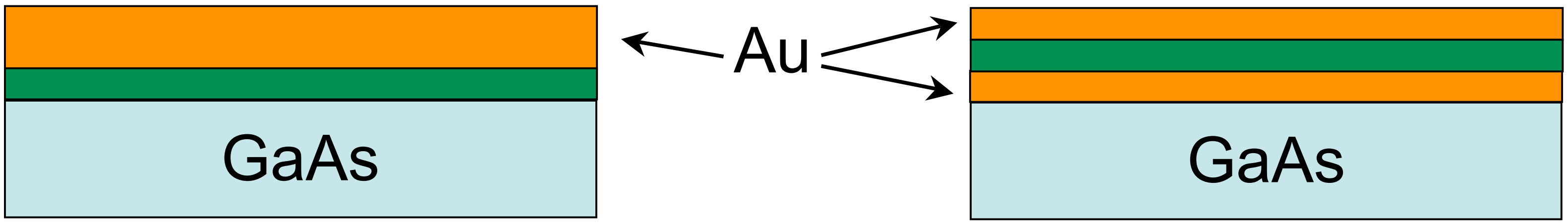
- Au-S vs. Au-CH_3
- Au can penetration through C16MT layer to GaAs interface
- Recent results indicate Au diffusing to GaAs interface (Cahen, Walker & Janes)
- Degree of penetration depends on evaporation conditions
- Expect less penetration for dithiol

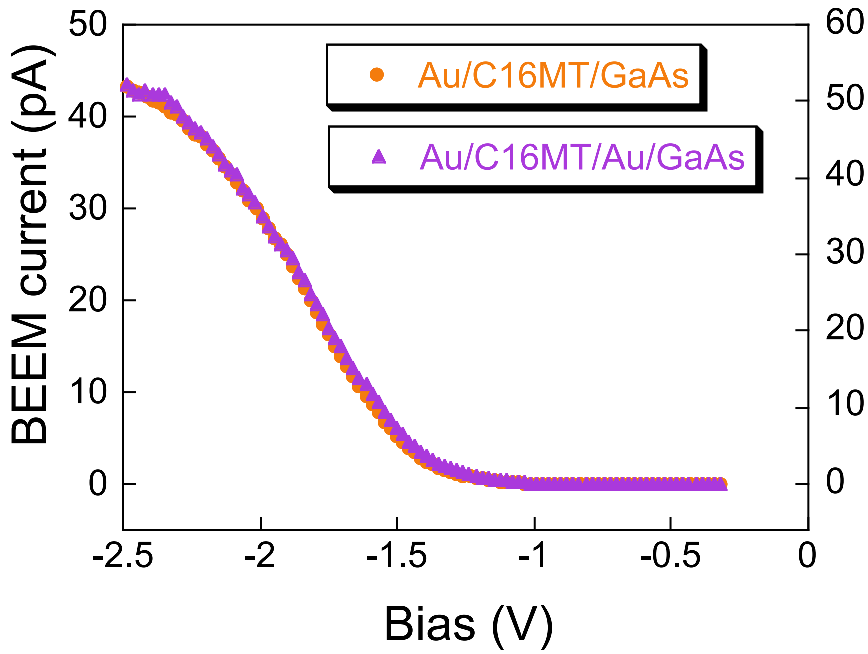


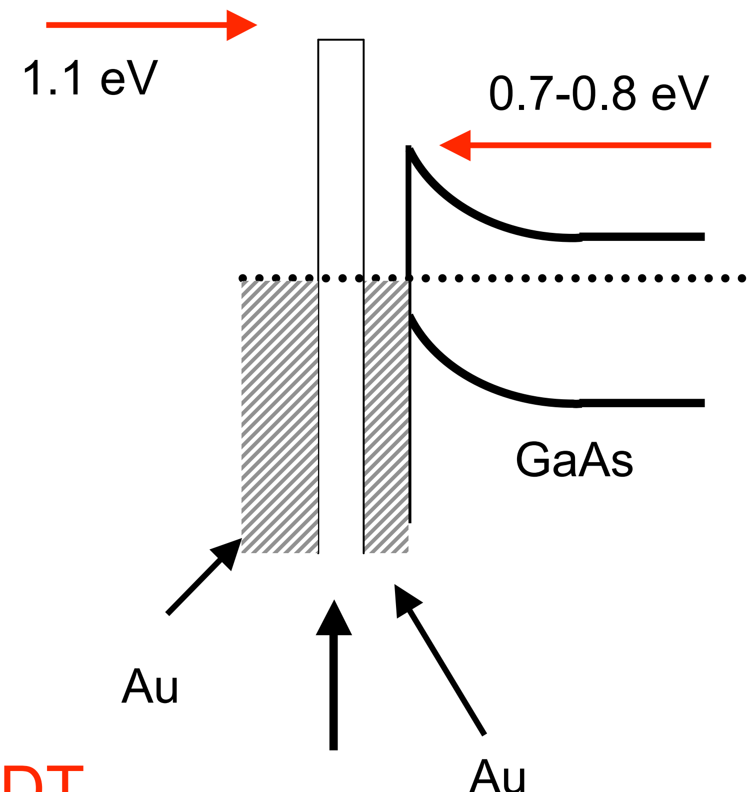
Haick, JPCB 109, 9622 (2005)



BEEM of Au/molecule/Au/GaAs

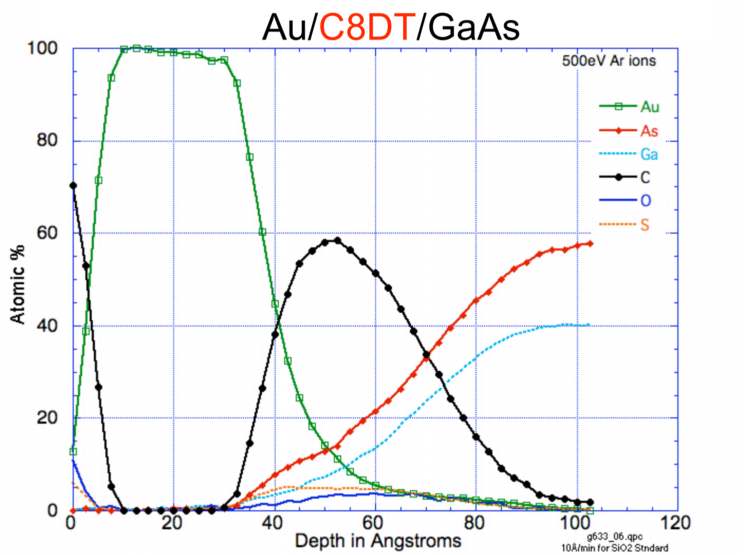


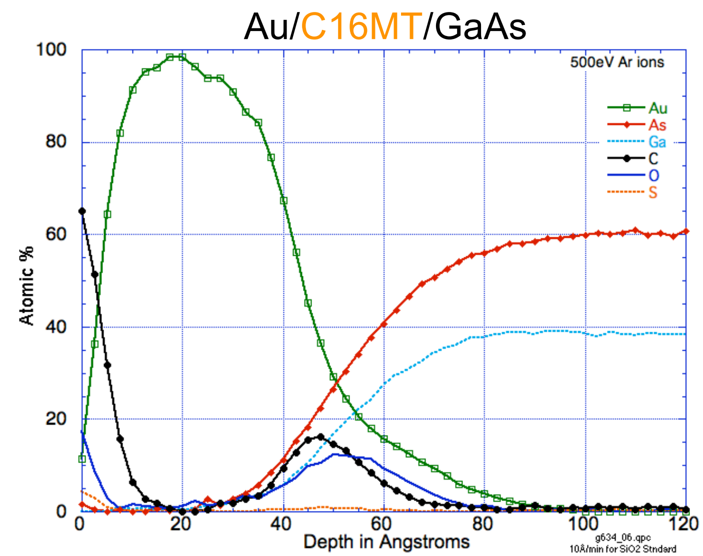


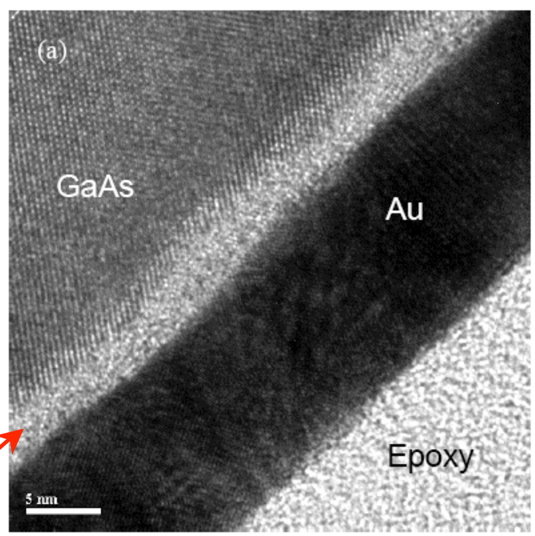


Au penetrates C16MT, but not C8DT

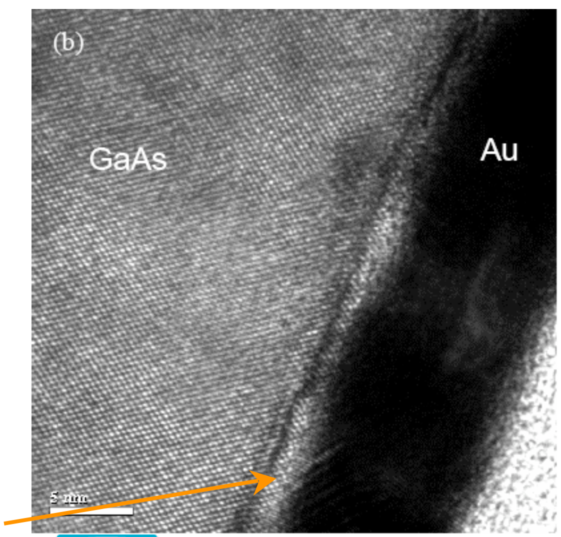
Structural Characterizaiton of Diodes







C8DT



C16MT

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Summary

- SAM formation on GaAs ≠ on Au; Thiol ≠ dithiol
- Schottky barrier height much lower from I-V-T measurements than RT I-V using theoretical A**; A** much smaller than ideal value
- First BEEM measurement on molecular diodes
  - BEEM threshold (1.5 eV) > I-V barrier height (0.7-0.8 eV)
  - Ballistic transport through LUMO (or lowest unoccupied interfacial states)
  - Au penetration in C16MT: lower BEEM threshold due to inhomogeneous junctions
- Low transmission in Au/C8DT/GaAs
  - Also low in A**; BEEM following the same trend as I-V-T
  - Disordered S-GaAs interface?
  - Interfacial charges/dipoles?
  - Tunneling through insulating layer?