Supporting Materials

Molecular Self-Assembly at Bare Semiconductor Surfaces: Cooperative Substrate-Molecule Effects in Octadecanethiolate Monolayer Assemblies on GaAs (111), (110), and (100)

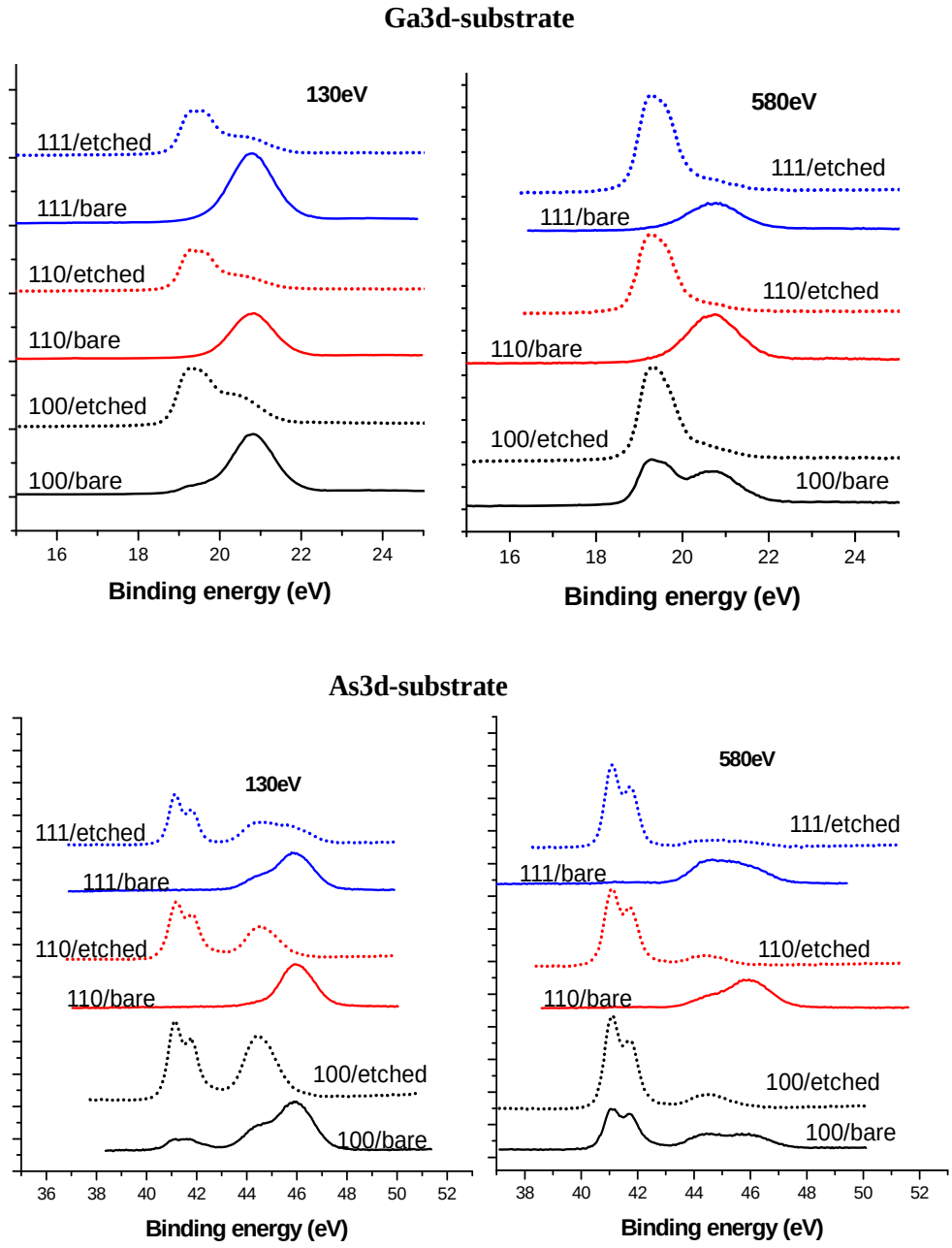
Christine L. McGuiness,[+1] Gregory A. Diehl,[1] Daniel Blasini,[2] Detlef-M. Smilgies,[3] M. Zhu,[5] Nitin Samarath,[5] Tobias Weidner,[#,4] Nirmayla Ballav,[4] Michael Zharnikov,[4,] David L. Allara[1,*]*

[1]Departments of Chemistry and Materials Science & Engineering, The Pennsylvania State University, 104 Chemistry Building, University Park, PA 16801-6300
[2]Department of Chemistry, Cornell University, Baker Laboratory, Ithaca NY 14853-1301
[3]Cornell High Energy Synchrotron Source, 200L Wilson Lab, Ithaca, NY 14853.
[4]Angewandte Physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 253, D-69120 Heildelberg, Germany
[5]Department of Physics, The Pennsylvania State University, 104 Davey, University Park, PA 16801-6300

*Corresponding Author Email: dla3@psu.edu
+ Present address: Plextronics, Inc. 2180 William Pitt Way, Pittsburgh, PA,15238, USA
# Present address: National ESCA and Surface Analysis Center for Biomedical Problems (NESAC/BIO), University of Washington, Seattle, WA 98195, USA

S1 Ga 3d and As 3d HRXPS of freshly etched and bare, air exposed GaAs(001) substrates

Etching was done by immersing the substrates in concentrated NH_4OH for 1-5 minutes. Immediately after immersion, the sample was rinsed with anhydrous ethanol, dried with an N_2 stream and transferred into the XPS analysis chamber. The air exposed samples were placed in a closed wafer container for up to a few days before loading in the XPS chamber. The spectra are stacked by arbitrary count offsets for purposes of display. In all cases the bare, exposed spectra show a distinct, strong growth of oxide peaks at high binding energies. Comparable storage of ODT SAM samples show only minor oxide related peaks (see main article text).



S2 Contact angle, IRS and XPS measurements on epi-GaAs(001) substrates

Advancing contact angle measurements (θ_a) and associated hysteresis values ($\Delta\theta$) were also made for **ODT** SAMs on the epitaxial-GaAs (001) surface. For H_2O probe liquids, $\theta_{a\text{-}H2O}$ =112(±3)º and $\Delta\theta_{\text{-}H2O}$ = 11(±3)º were found. For HD probe liquids, $\theta_{a\text{-}HD}$ = 36(±1)º and $\Delta\theta_{\text{-}HD}$ = 4(±1)º were found. These measurements are, within error, the same as the contact angle measurements made for **ODT** SAMs on GaAs (001),[1] (110) (111B)-As surfaces.

Infrared spectroscopy measurements of **ODT** SAMS on the epitaxial GaAs (001) surfaces made at 55º AOI (see Figure S2-1) show modes that appear at the same frequencies as the **ODT** SAMS on GaAs (001) indicative of a high degree of conformational ordering, 2850 cm^{-1} [$-CH_2-$ sym str (d^+)], 2878 cm^{-1} [CH_3 sym str (r^+) split by Fermi Resonance (FR) interaction with the CH_3 asym def], 2918 cm^{-1} [$-CH_2-$ antisym str (d^-)], and 2965 cm^{-1} [CH_3 asym in-plane str (r_a^-)].

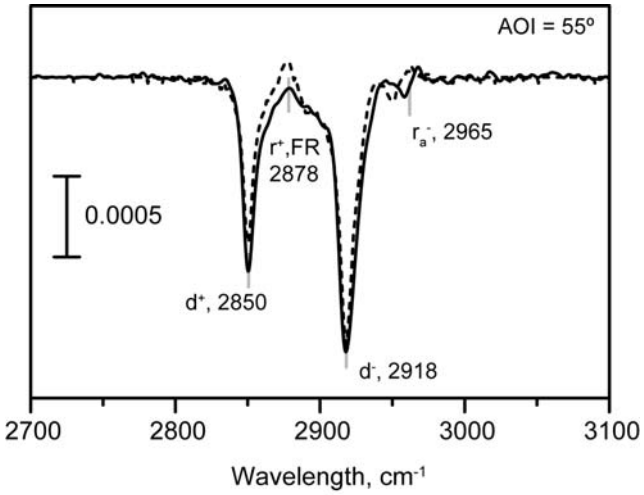


Figure S2-1. IRS Spectrum of for **ODT** molecules assembled on epitaxial-GaAs (001) taken at an angle of incidence (AOI) of 55º. Simulated IRS spectra using a 2 chain per unit cell model with chains in an all-trans configuration (dotted lines). For details of the simulations see the main article.

At a 55º AOI, the d^+ and d^- modes for the **ODT** SAMS on the epitaxial-GaAs surface have negative absorbance features, consistent with the inversion in the direction of transverse (TO) absorption intensities around Brewster's angle (θ_B=73.2°for GaAs) from positive ($\theta > \theta_B$) to negative ($\theta < \theta_B$) on dielectric surfaces. Using the organization of **ODT** SAMS on GaAs (001) surfaces as a model, the IRS spectra were simulated using the 2 chain/unit cell structure. The best fit for the **ODT**/epitaxial-GaAs (001) system was obtained with an ideal all-*trans* 2 chain model with chain tilt, Φ =-15 º and twist, ψ = 43 º and 133 º, the same fit as the **ODT**/GaAs (001) SAMs (see Fig. S2-1 and the main article).

Comparison of the O1s, C1s and S2p core level spectra for **ODT** SAMs on epitaxial-GaAs (001) and GaAs (001) surfaces showed that, within the resolution limitations of this techniques (~1 eV resolution compared to ~0.7 eV for HRXPS measurements) no differences in the chemical bonding of the **ODT** SAMs to the two surfaces were observed (see Figure S2-2). From the O1s spectra, it can be seen that only a very small amount of residual oxide remains on the surface, showing that the **ODT** SAMs are able to protect both underlying GaAs substrate from oxidation and degradation. Furthermore, the formation of the thiolate bond to the substrate for both surfaces is identical, as exhibited in the S 2p spectra of **ODT** SAMs in Fig. S2-2. In both S 2p spectra, a single doublet at a characteristic binding energy of about 162.3 eV (S $2p_{3/2}$) is observed. In addition, the S 2p spectra were curve fit to show the contributions of the other component features including the Ga 3s peak (160 eV) which dominates the contributions and an As 3p plasmon features which is required to obtain good fits. These fits are consistent with previously reported S 2p spectra for **ODT** SAMs on GaAs (001) surfaces.[1] In addition, the As 3d and Ga 3d spectra for the **ODT** SAMs on both surfaces were indistinguishable.

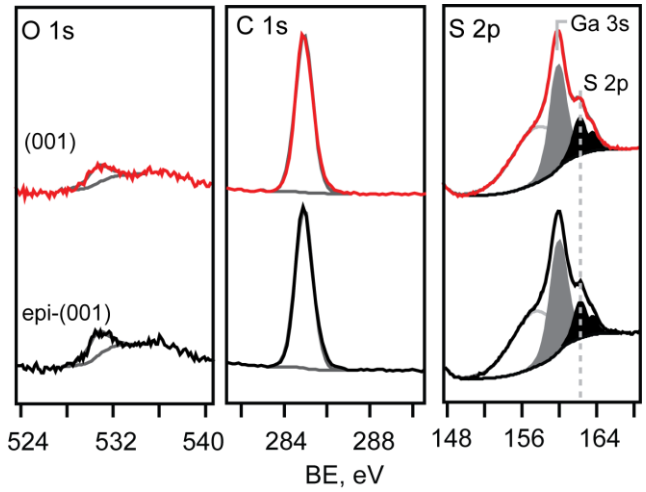


Figure S2-2. Comparison of the XPS O 1s, C 1s and S 2p spectra on the GaAs (001) and epitaxial-GaAs (001) surfaces after **ODT** monolayer formation.

References

1 McGuiness, C. L.; Shaporenko, A.; Mars, C. K.; Uppili, S.; Zharnikov, M.; Allara, D. L. Molecular Self-Assembly at Bare Semiconductor Surfaces: Preparation and Characterization of Highly Organized Octadecanethiolate Monolayers on GaAs(001), *Journal of the American Chemical Society* **2006**, *128*, 5231-5243.