

Influence of Interfacial Chemistry and Molecular Length on the Electronic Properties of Metal-Molecule-Silicon Junctions Produced by Flip Chip Lamination

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The integration of organic molecules with silicon is increasingly being studied for potential uses in hybrid electronic devices. However, creating a dense and highly ordered organic monolayer on silicon with reliable metal-molecule contacts still remains a challenge. A novel technique, flip chip lamination (FCL), has been developed to create uniform, covalently bound metal-molecule-semiconductor junctions using nanotransfer printing.^[1, 2] FCL is advantageous because it is a versatile technique that can be used for a variety of molecules, the molecular structure can be interrogated while in the device architecture, and it is a low cost scheme that preserves the integrity of the molecular self-assembled monolayers (SAMs) within the junction. This work reports on studies of several molecular SAMs to investigate the role of length dependence and molecular structure for metal-molecule-silicon junctions. The effects of the FCL process on the chemical and physical properties of the embedded molecular layer were examined with p-polarized backside reflectance absorption infrared spectroscopy (pb-RAIRS), spectroscopic ellipsometry, and water contact angle measurements. Electrical measurements were performed to characterize the electronic properties of the organic SAMs and to offer better insight into the mechanisms at play in the electronic transport through the metal-molecule-silicon junction.

The molecules used in this study, as seen in figure 1, were dithiol molecules, 1,16 hexadecane dithiol (HDDT), 1,10 decane dithiol (DDT), 1, 8 octane dithiol (ODT), and 4,4'-*para*-terphenyldithiol (TPDT). Figure 2 shows pb-RAIRS data for the molecular monolayers following the FCL procedure. The data for the alkyl chain molecules (HDDT, DDT, and ODT) in figure 2a reveals important information about the molecules in the junction. Peaks are observed at $\approx 2924\text{ cm}^{-1}$ for all these molecules, which corresponds to the $\nu_{\text{as}}(\text{CH}_2)$ mode, and indicates that the structure of the molecular films within the junction is well maintained following the FCL procedure. The pb-RAIRS for the TPDT molecule (figure 2b), which is made of aromatic rings, exhibits peaks at 1479 cm^{-1} and 1001 cm^{-1} (19a and 18a mode using Wilson notation) assigned to $\nu(\text{C}=\text{C})$ aromatic ring modes and a peak at 808 cm^{-1} (10) assigned to $\nu(\text{C}-\text{H})$ ring mode consistent with an aromatic ring structure. After lamination, the spectra contain the same peaks somewhat broadened, indicating a decrease in homogeneity within the molecular structure of the FCL junction. The observation of similar peaks in the gold free-standing monolayers and within the molecular junction indicates that the molecular structure remains intact with some likely reorientation.

Current-voltage measurements of molecular electronic devices made using the various molecular SAMs were also taken (figure 3). An exponential dependence on molecular length is observed in the current-voltage data for the HDDT, DDT, and ODT molecular devices. At high forward bias, where the tunneling across the molecular junction is expected to dominate the transport properties, TPDT shows higher current compared with DDT, which has a similar molecular length. The effect of the π -conjugation, which is expected to exhibit higher currents due to the extended π -orbitals, in the TPDT molecules is observed in this high bias regime. The difference observed in this system is not as large as expected. This is possibly due to the lower molecular density and less ordered TPDT monolayers when compared with the alkanethiols. Transition voltage spectroscopy (TVS) measurements were also studied. TVS provides information about the height of the energy barrier for the molecules.^[3] The transition voltage for the HDDT, DDT, and ODT molecules are found to be approximately the same, which is expected since the molecules all have same energy gap. The TPDT value is found to be lower due to the lower energy barrier, though not as low as expected most likely due to the lower quality monolayer attributed with the TPDT SAMs.

This work investigates hybrid silicon-molecule devices using FCL, a novel new technique for fabricating the devices. FCL allows for both structural and electronic characterization of the devices within the device architecture. This work studies at a variety of molecules with varying lengths and backbone structures and provides a method to better understand charge transport through molecular electronic devices.

References

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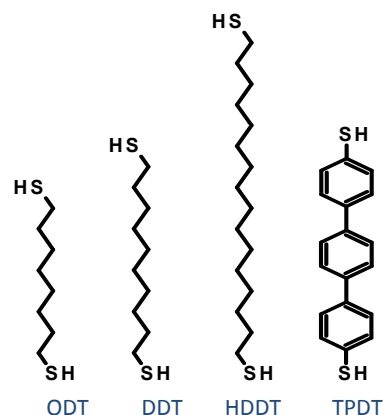


Figure 1: Molecules used in this work to fabricated FCL junctions.

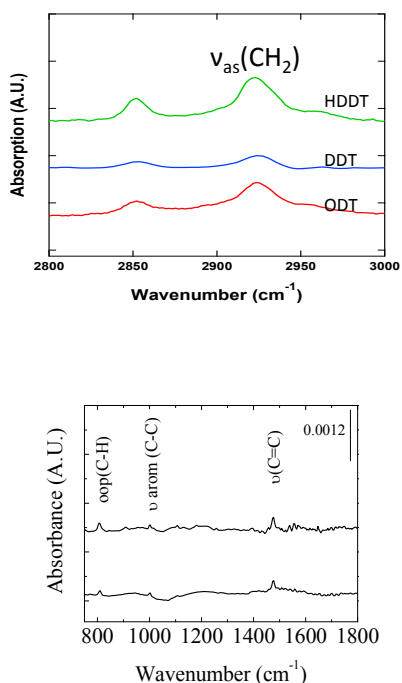


Figure 2: (a) pb-RAIRs for HDDT, DDT, and ODT molecules. (b) pb-RAIRs for TPDT molecular SAMs both prior to and after lamination.

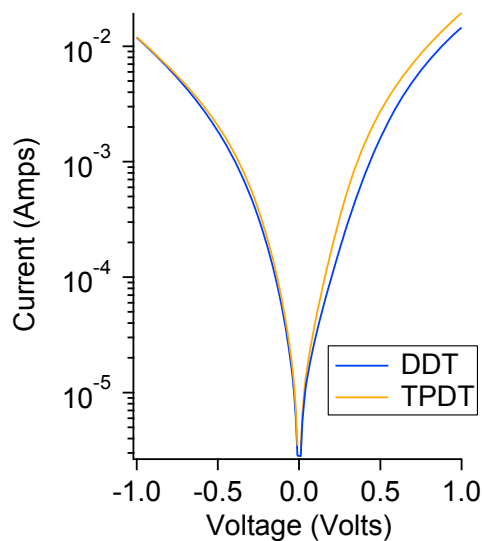
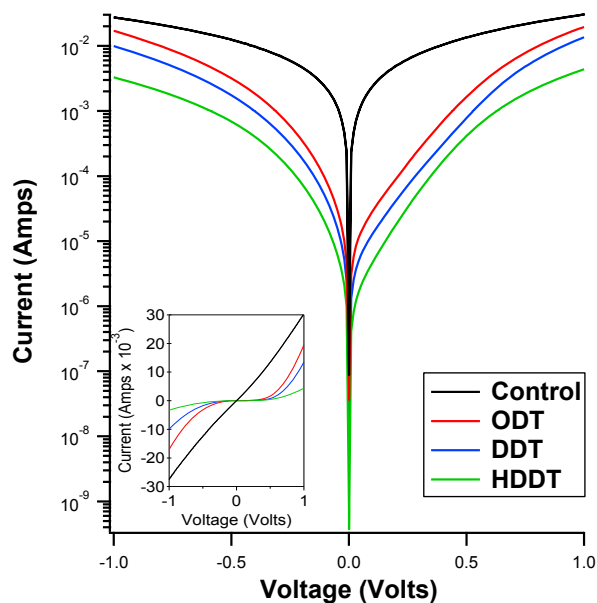


Figure 3: (a) Current-voltage curves for the ODT, DDT, and HDDT molecules along with a silicon control. The exponential dependence of current due to molecular length is observed. (b) Current-voltage curves for TPDT and DDT molecules. The TPDT shows a larger current at high positive bias due to the π -conjugation of the molecules.