

Metal-Molecule-Silicon Junctions Produced by Flip Chip Lamination of Dithiols: Effect of Molecular Length and Backbone

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The integration of organic molecules with silicon is increasingly being studied for potential uses in hybrid electronic devices. Creating dense and highly ordered organic monolayers on silicon with reliable metal contacts still remains a challenge. A novel technique, flip chip lamination (FCL), has been developed to create uniform metal-molecule-semiconductor junctions. FCL uses nanotransfer printing to covalently attach self-assembled monolayers to a hydrogen-passivated Si(111) surface. Several dithiol molecules were studied to explore the role of molecular length and chemical structure on the physical and electronic properties of the molecules. The effects of the FCL process on the chemical and physical properties of the imbedded molecular layer were interrogated with p-polarized-backside reflectance absorption infrared spectroscopy. Electrical measurements were also performed to characterize device structure and to offer better insight into the mechanisms at play in the electronic transport.

Introduction

Organic molecules are of great interest for nanoelectronic applications because they are a versatile material which can be used to make devices, such as photovoltaics, chemical and biological sensors, or transistors (1-4). The integration of organic molecules with silicon is particularly interesting due to the many advantages these hybrid devices can offer for post-CMOS technology (5, 6). For example, organic molecules can incorporate new functionality with conventional silicon technology. Additionally, the covalent binding of the molecules to silicon is well understood and forms robust monolayers (7, 8). Moreover, the ability to control the doping of silicon allows the band structure to be tuned and can enable non-linear transport behavior (9, 10). Finally by combining the organic functionality with silicon, the processing expertise and knowledge base of the microelectronics industry can be utilized for creating the next generation of devices.

Despite the potential of silicon-based molecular electronics, fabrication of the devices still presents difficult challenges. Issues such as electrode surface roughness, molecule-electrode connection, and physical structure of the molecular packing all are important factors when creating devices. Forming dense, ordered molecular monolayers on silicon

is also a very challenging aspect of fabrication. The strong covalent bonding on the silicon surface limits the mobility of the molecules. Therefore, self-assembled monolayers (SAMs) formed on the hydrogen passivated Si(111) surface tend to have lower densities and are more disordered than SAMs formed on gold surfaces. For semiconductors, this is particularly problematic since the semiconductor surface remains susceptible to further reactions such as oxidation and the monolayer interface termination may not be sufficient to electrically passivate the surface states. Additionally, since the silicon surface is very reactive, selective attachment of bifunctional molecules has proven difficult to achieve (11). Fabrication of the metallic top contact, for instance, can cause damage to the molecular layer, create pin holes, or electrically short the device (12, 13).

In order to address these concerns a novel fabrication technique, flip-chip lamination (FCL), was developed to create ordered, dense organic monolayers covalently bound between gold and semiconductor electrodes (14). This procedure takes advantage of well established thiol-gold chemistry and combines it with nanotransfer printing (nTP) in order to make reliable molecular junctions. In the FCL procedure, dense, highly ordered SAMs of ω -functionalized thiol molecules are formed on ultrasmooth gold (uSAu) surfaces. The SAMs are then covalently bound to silicon by applying temperature and pressure during the nTP step. This procedure not only creates a well ordered metal-molecule-semiconductor junction, but it also provides a reliable test bed to study both the physical and electronic properties of a wide range of molecular junctions.

This study focuses on the physical and electrical properties of two dithiol molecules (Figure 1), decanedithiol (DDT) and 4,4'-*para*-terphenyldithiol (TPDT), formed into the previously described metal-molecule-semiconductor structure by using FCL. Infrared spectroscopy (IR) measurements probe the conformation of the molecular monolayers following FCL and reveal the integrity of the SAMs is maintained. Current-voltage measurements show a dependence both on the structure of the molecules as well as the molecular length. Dithiol molecules were chosen because the bonding at the interface is constant allowing one to investigate the electronic contribution due to the structure of the molecules. Self-assembly of thiol-functionalized molecules on gold is well understood, however, the reaction of thiols on silicon is less-well studied.

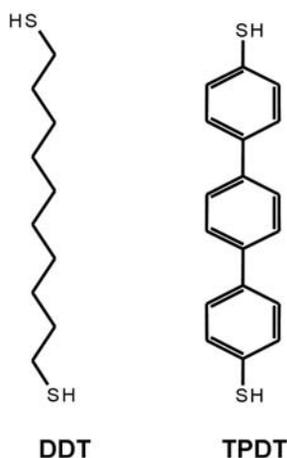


Figure 1. Structure of the two molecules tethered to Si and Au using the FCL procedure.

Experimental Methods

Flip Chip Lamination

The FCL procedure, depicted in Figure 2, begins with the formation of uSAu films by evaporating 100 nm of gold onto a native silicon-oxide substrate treated with a fluorinated release layer. The uSAu film is then transferred onto a polyethylene terephthalate (PET) substrate via nTP at conditions of 90° C and 2 MPa. The DDT and TPDT monolayers are then prepared on the uSAu films. The gold films are first cleaned for 10 minutes in UV-ozone followed by rinsing with ethanol. The DDT substrates are then placed in a 10 mMol/L ethanolic solution and the TPDT substrate in a 1 mMol/L ethanolic solution for 4 hours. Solution concentrations and soaking times were optimized to achieve reproducible high-quality monolayers. After removing the samples from the solution, they are carefully rinsed with ethanol and isopropanol and dried with N₂ gas. The samples were characterized with infrared spectroscopy to ensure a high-quality monolayer.

The exposed molecular functional group of the thiol-monolayer is then laminated to a hydrogen passivated Si(111) substrate. The silicon surface is hydrogen-terminated by submerging the Si substrate into a cleanroom grade buffered oxide etch (6:1, NH₄F:HF) for 30 s. After passivation, the silicon samples are rinsed with DI water and dried with N₂ gas. The Si and molecule-uSAu substrates are then placed into contact and exposed to the lamination conditions of 90° C and 4 MPa for 5 min for each molecular monolayer. These conditions were optimized for adhesion of the Si-H and the dithiol molecules.

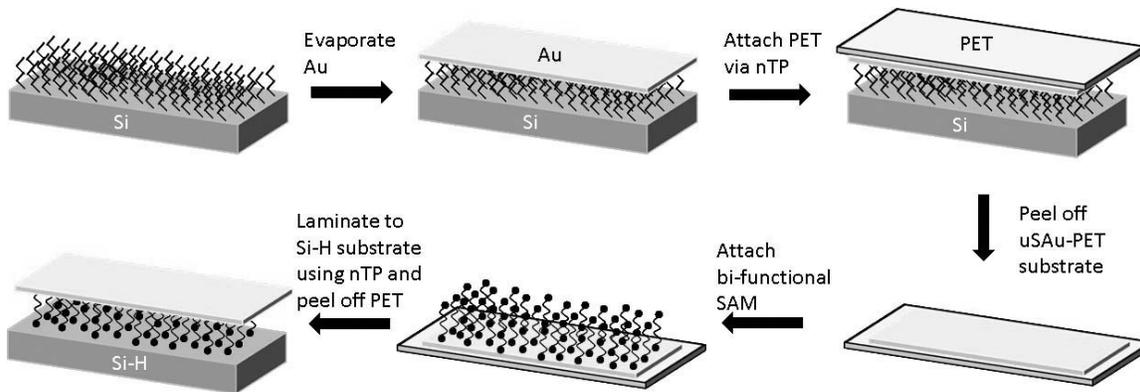


Figure 2. A schematic of the FCL procedure. Gold is evaporated onto a silicon substrate functionalized with a fluorinated release layer. Using nTP, the gold film is transferred to a PET substrate. A bi-functional molecular monolayer is then attached to the gold film via a thiol linkage. The molecular monolayer on gold is then flipped and covalently attached to a hydrogen-passivated silicon substrate by using nTP and the PET film is peeled away.

Physical and Electronic Characterization

The structure of free-standing monolayers on uSAu were characterized by Fourier transform infrared spectroscopy (FTIR) using a commercial Fourier-transform infrared spectrometer with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector

(600 cm^{-1} to 4000 cm^{-1}) set to 8 cm^{-1} resolution. The angle of incidence was 70° from the surface normal. Freshly cleaned uSAu/PET and e-beam evaporated Au/H-Si were used as references for freestanding monolayers and FCL samples, respectively. The metal-molecule-silicon junctions were characterized by using p-polarized backside reflection absorption spectroscopy (pb-RAIRS) taking advantage of the infrared-transparent properties of silicon to investigate the interfacial and molecular structure within the metal-molecule-silicon junction (15, 16).

Two-terminal electrical characterization was performed by using a commercial probe station. The measurements were performed on patterned uSAu/molecule/Si junctions with areas of $\approx 50 \mu\text{m}$ by $50 \mu\text{m}$. The patterns were made via shadow mask during the gold evaporation. Also for samples prepared for electrical characterization, the evaporated gold substrates were placed in an ethanol solution with a fluorinated thiol molecule prior to the lamination to the PET. This additional step is taken to decrease the surface free energy of the gold, which allows the flexible substrate to be removed following the FCL procedure and the electronic properties of the molecular layers to be interrogated.

Results and Discussion

Infrared Spectroscopy

Infrared spectroscopy was used to probe the conformation of the molecular layer prior to junction formation and within the FCL-fabricated metal-molecule-silicon junction. Figure 3 shows representative IR spectra from the free-standing monolayers on uSAu and within the metal-molecule-silicon junction. In the spectra obtained from DDT, the $\nu_{\text{as}}(\text{CH}_2)$ mode appears at 2927 cm^{-1} in the free-standing monolayer on uSAu and after molecular junction formation, this mode shifts to 2924 cm^{-1} . The energy of this mode in molecular layers is related to the order of the aliphatic chains with a shift to lower energy consistent with removal of gauche defects within the molecular backbone (17, 18). The TPDT molecule exhibits peaks at 1479 cm^{-1} and 1001 cm^{-1} (19a and 18a) assigned to $\nu(\text{C}=\text{C})$ aromatic ring modes and a peak at 808 cm^{-1} (10) assigned to $\delta(\text{C}-\text{H})$ 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 uSAu free-standing monolayers and within the molecular junction indicates that the molecular structure remains intact with some likely reorientation.

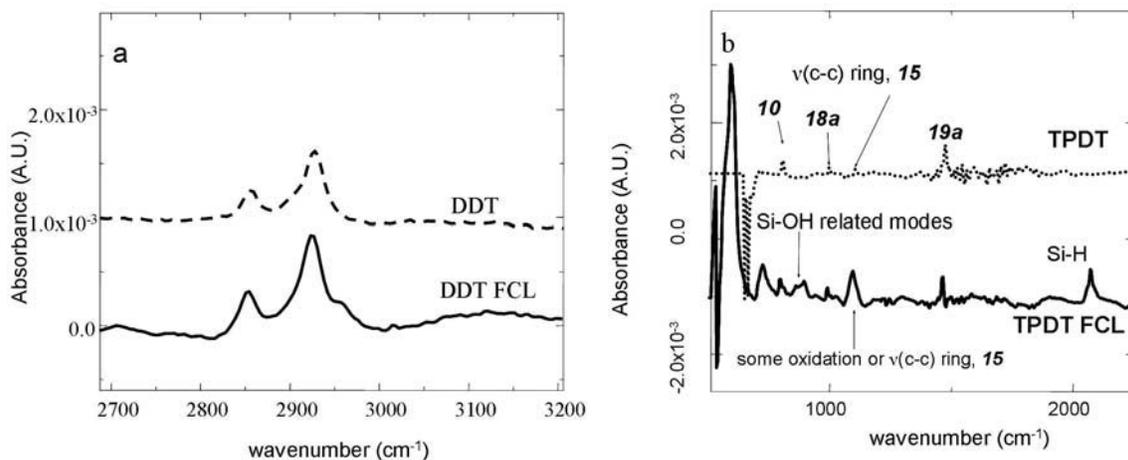


Figure 3. (a) pb-RAIRS data for DDT monolayer before and after FCL. (b) pb-RAIRS data for the TPDT monolayer before and after FCL.

The observation of similar molecular conformation within the junction following FCL is consistent with previous studies of COOH-terminated alkyl molecules used in FCL (14, 19). Bonding of the thiol-linkage to the H-terminated silicon surface is thought to occur through a Si-S linkage. The absence of a Si-S infrared mode is not unexpected as this IR mode is weak and appears at energies lower than our spectral range. It appears that some of the Si-H is consumed during the lamination process as the $\nu(\text{Si-H})$ mode at 2084 cm⁻¹ exhibits a $\approx 40\%$ area reduction within all of the dithiol junctions compared to a freshly etched H-Si sample. Additionally, there are no SiO₂ vibrations observed in the 1000 cm⁻¹ to 1200 cm⁻¹ region for the DDT monolayers which confirms that there was no oxidation of the silicon substrate during the procedure because of the molecular monolayer. A small peak is observed for the TPDT monolayers at 1100 cm⁻¹ but this is attributed to the lower density of the monolayer and no S-O modes are observed. The absence of the S-O infrared modes, the observations of the SiO₂ vibrations within the junction, and the reduction of the Si-H suggest adhesion of the monolayer to the Si surface occurs through a Si-S linkage.

Thiols have been shown to attach to silicon in UHV predominately through cleavage of the S-H bond and formation of Si-S and Si-H surface species (20, 21). Previous work has reported solution-based thiol attachment to H-terminated silicon (22-24). Comparison of the solution-formed monolayers from thiol- and alcohol-terminated aliphatics with H-Si indicated both molecules react with the H-Si in a similar fashion with the thiol forming slightly less dense monolayers. It is suggested the thiols bond through a nucleophilic attack of the Si-H surface similar to the case observed for alcohols where the oxygen lone pair electrons react with the Si-H leading to a Si-O-R linkage and loss of dihydrogen (25, 26). In the case of the FCL-fabrication described here, the monolayers are preformed with the exposed thiol group in contact with the H-Si surface under applied pressure and temperature. Adhesion of the two substrates doesn't occur until relatively higher pressure and temperature, compared with previous lamination conditions for alkene and carboxylic acid-terminated monolayers(14, 27, 28). This may be indicative of the thiol-silicon bonding requiring more energy. Alternatively, the FCL-technique does not allow for the escape of evolved hydrogen gas, which may obstruct

some of the reactive sites leading to the larger temperature and pressure conditions necessary for adhesion.

Electrical Characterization

In order to assess the electrical properties of the molecular junctions following the FCL procedure, current-voltage data were taken for the DDT and TPDT molecules, as seen in Figure 4. In these experiments n-type Si(111) substrates with a $\rho = 0.001 - 0.005 \Omega\text{-cm}$ were used. The silicon substrate was grounded and the bias was applied to the top metal electrode. The currents observed for the molecular junctions are strongly attenuated compared to the metal-silicon control, also shown in Figure 4. This behavior is consistent with the molecular component acting as an ultra thin dielectric layer.

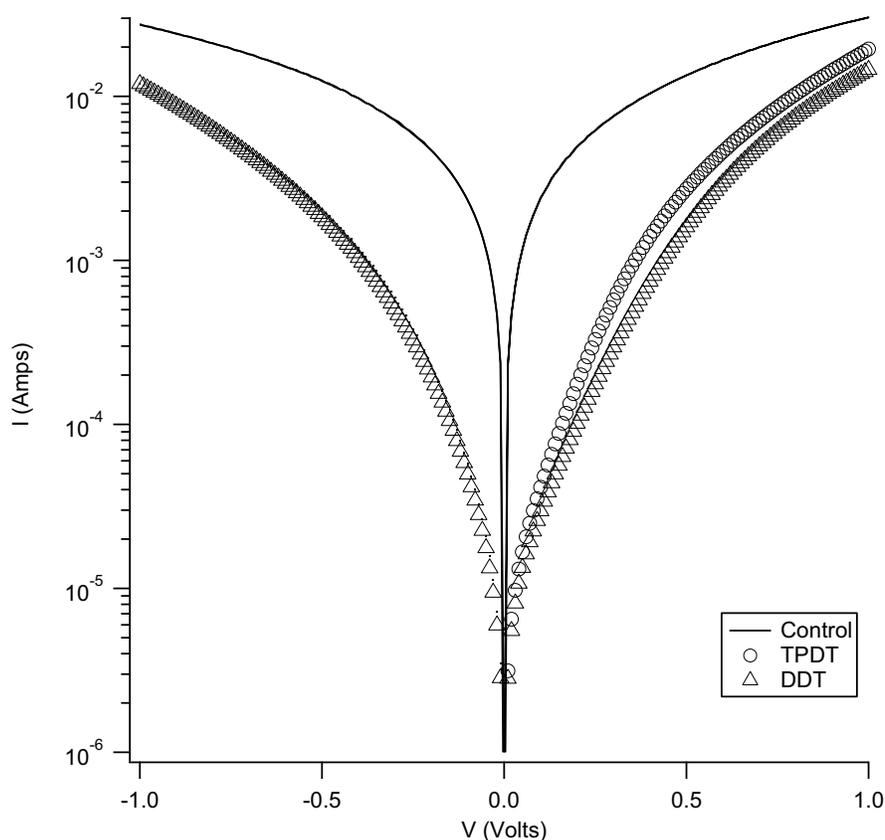


Figure 4. Current voltage curves for the DDT and TPDT molecules in a Au-molecule-Si junction produced by FCL. A current voltage curve is also included for a control sample with Au evaporated directly onto the Si-H sample.

The I-V curves show a lower current for both molecular species within the junction as compared to the silicon control sample indicating that the SAM layers play a role in the charge transport. 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. 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 (29). 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 alkanedithiols. Other longer alkyl chain dithiols have also been studied and they show lower currents as expected (30). Further electrical studies are underway, including temperature-dependence measurements to better understand the effects of the molecular layer.

Conclusions

This study demonstrates the usefulness of FCL to create metal-molecule-semiconductor junctions with dense and highly ordered films covalently bound at both ends. Infrared spectroscopy shows that the molecular junctions of the DDT and TPDT molecular conformation remain intact following FCL. Current-voltage measurements of the monolayers show that the TPDT molecules produce the highest currents in the direct tunneling regime due to the extended π -conjugation of the molecule, though the current is not as high as expected possibly due to the lower density and higher disorder of the monolayer. FCL can be used as a test bed to investigate the physical and electrical properties of the molecular junctions and has the potential to impact the field of organic electronics and many applications.

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