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## Metrology of Molecular Devices made by Flip Chip Lamination

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Scaling of conventional electronics has continued unabated to dimensions approaching fundamental physical limits. As technology continues to evolve there are increasing demands to identify alternate routes of performing electrical functions. One novel device architecture is molecular electronics. The fabrication and metrology of molecular based devices has progressed but remains challenging. We have focused our efforts on silicon-based molecular electronic devices and developed a crucial understanding of the formation and characterization of molecular electronic devices. This paper gives an overview of our technology highlighting formation of monolayers and metallization of the monolayers. Characterization of metal-monolayer-silicon structures will be discussed throughout.

### Introduction

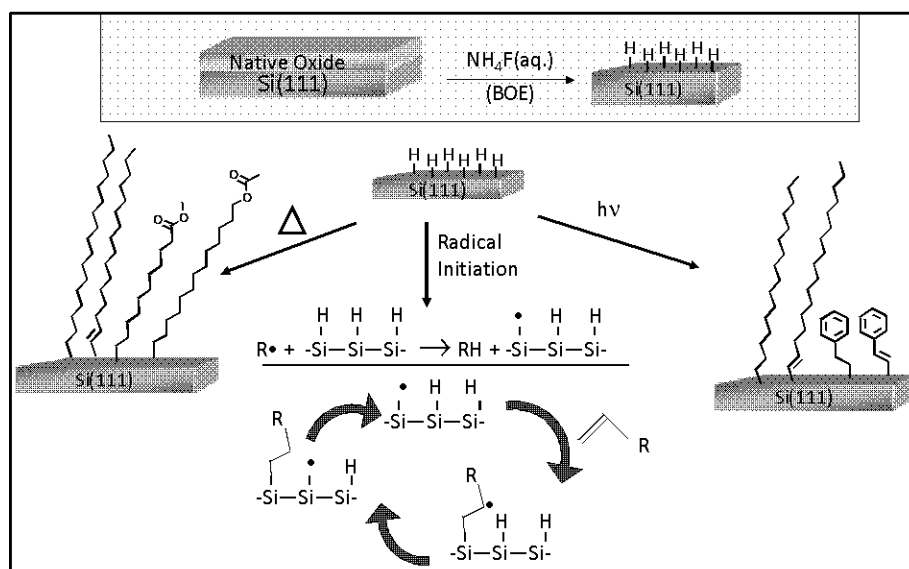
The concept of using molecules as electrical components originated in 1974 (1), but practical implementation remains a challenge. The use of molecules in electrical devices holds promise as they are small, discrete, and easy to synthesize and functionalize by using chemistry. For electronics applications, molecules can offer additional advantages other than their use as mere dielectric layers. Molecules can be used to modify the electrical properties of devices and their interfaces. Molecules can be used to add functionality to create sensors or scaffolding for patterning and complex design fabrication. Even with all of this promise putting molecules where one wants them and attaching electrodes remains the limiting challenge.

While surface sensitive techniques have advanced greatly in the last 35 years, verifying the structure of molecular layers within buried metal-molecule-semiconductor junctions remains a challenge. Electrical contacts are opaque to most optical and electronic probes, with one notable exception. Silicon is transparent in the infrared. By using a p-polarized backside reflection absorption infrared spectroscopic (pb-RAIRS) geometry, chemical and conformational changes at the interfaces and within the monolayers can be investigated (2-4). Two-terminal electrical measurements and depth-profiling x-ray photoelectron spectroscopy will also be addressed as a means to interrogate molecular junctions.

### Silicon-Focused Molecular Electronics

Silicon-focused molecular electronics are of significance from many different standpoints. First, silicon is the basis of the microelectronics industry providing a vast

knowledge base concerning the processing and building of electronic components. Incorporation of molecules with existing silicon-based devices may be used to fabricate hybrid systems with electrical properties determined by both the molecular layer and the semiconductor. Secondly, the semiconductor band structure can be used to take advantage of the molecule-silicon system. From a scientific perspective, silicon is a rich area of research due to the number of surface configurations and bonding arrangements. Silicon is a very reactive surface forming strong covalent bonds with most atoms making molecular attachment potentially robust and non-resistive. But the tradeoff from this strong surface bonding means there is almost no surface mobility of bound molecules making it impossible for the molecules to self-assemble and challenging to achieve dense monolayers. Finally from a practical perspective, silicon is transparent to infrared irradiation allowing one to use spectroscopy to characterize buried monolayers and interfaces within the same electrical device. Also, electrical devices composed of molecular components can be directly coupled with existing silicon microelectronic devices enabling more straightforward adoption of this emerging technology.

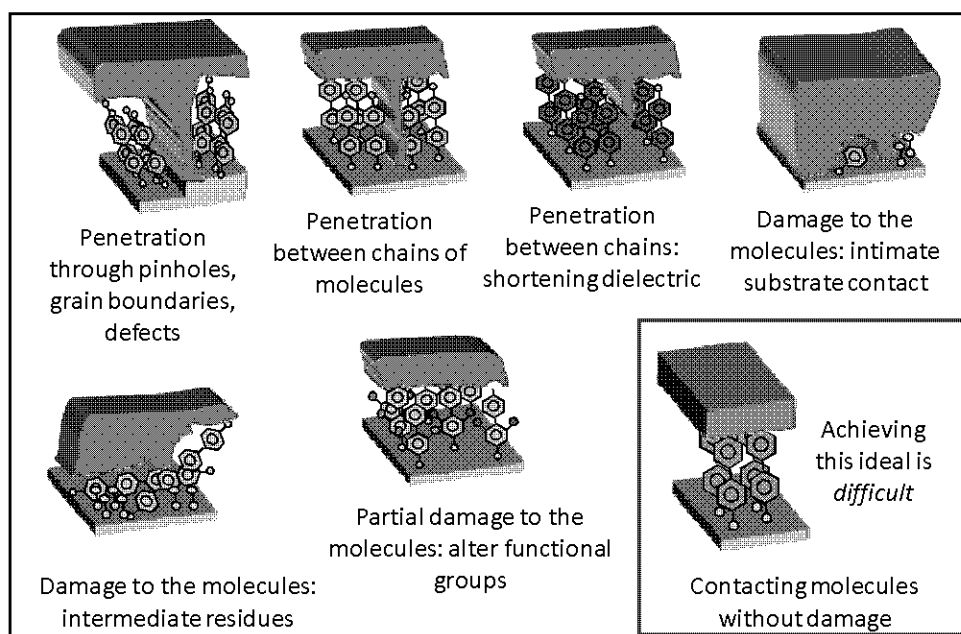


**Figure 1.** Ambient approaches to bonding molecules to silicon typically start with a hydrogen-terminated surface. The most prevalent approaches are the application of heat, light, or incorporation of a radical initiator.

Because silicon is quite reactive, ambient approaches to monolayer formation begin with passivation of the oxide stripped silicon surface typically with hydrogen or a halide such as chlorine (5-8). This passivation is typically done with the Si(111) surface by using a buffered hydrofluoric acid solution to take advantage of the anisotropic oxide etching properties which act to smooth the surface and result in a silicon monohydride (9). There are three primary approaches to forming the monolayers on the silicon surface including thermal, photon, or use of a radical initiator as shown in Figure 1. While the use of a radical initiator was among the first reports of molecules bonding to silicon (10), it is also among the most recent developments with diazo compounds being utilized to attach aromatic species to the surface (11-13) as well as being used to activate the silicon surface for the chemical attachment of other molecular species (14). All of these routes aim to tailor the surface reactivity to create a uniform dense film, crucial for molecular electronic applications.

### Intrinsic Properties at Nano-Dimensions

In order to measure the electrical response of molecules, it is necessary to confine the organic monolayers between two electrodes. While scanned probe techniques work well for isolated measurements, they are impractical for electrical devices and can suffer from extraneous environmental effects leading to varying results (15, 16). Ultimately, the ideal structure would consist of an atomically flat substrate with a dense well-ordered molecular layer onto which an atomically smooth top electrode is placed that can be wired to the macroscopic world. Unfortunately, achieving this ideal is quite difficult. Instead of a robust molecular junction, application of a top metal electrode can result in shorting or damage to the molecular layer through numerous pathways as shown in Figure 2. Metal can penetrate through pinholes, grain boundaries, and defects in optimal films or between molecular chains in less dense monolayers. Metal can damage the molecules resulting in shorting, fragmented molecular residues, or slightly altered molecular functional groups. These pathways can result in a variety of molecular junctions with widely varying properties due to differences in intrinsic chemical details at the nanoscale. Thus, it is imperative to characterize the chemical, physical, and electronic properties of the organic monolayers, electrodes, and metal-molecule-substrate junctions to understand the configuration and support rational design for desired function.



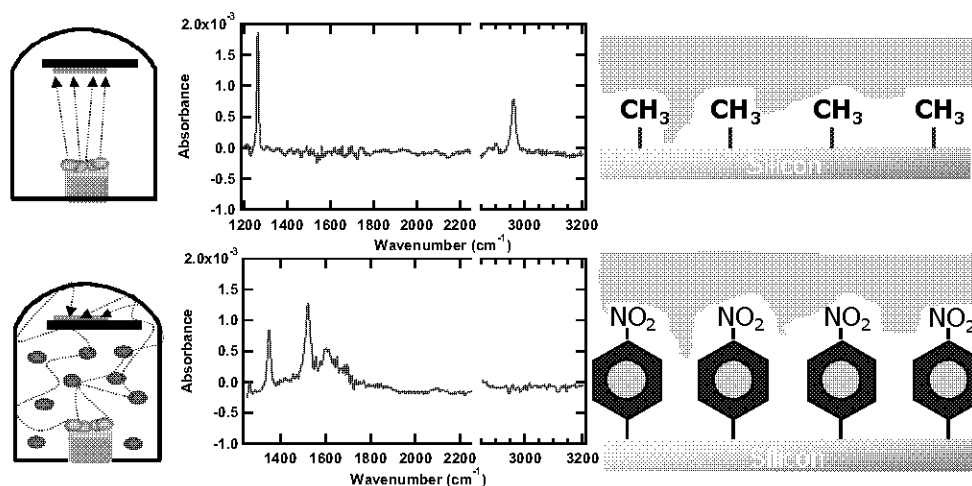
**Figure 2.** Metallization of molecular layers can result in a number of different products. The ideal product is a molecular junction between two ultrasoft electrodes but instead metal often damages the molecular layer. Metal can penetrate through pinholes, grain boundaries, and defects in optimal films or between molecular chains in less dense monolayers. Metal can damage the molecules resulting in shorting, fragmented molecular residues, or slightly altered molecular functional groups.

Thorough characterization of the electrodes and monolayers prior to assembly is possible by using nearly all conventional surface selective techniques. However,

characterization of the assembled junction is more demanding with the top electrode opaque to most surface sensitive techniques. Typical approaches to deal with this issue are the use of very thin top electrodes or destructive depth profiling techniques which can interrogate the interface but may give unreliable results due to contamination or fragmentation products. The better solution is to use a transparent electrode, such as silicon, which allows the nondestructive characterization of the buried molecular junction by infrared irradiation of molecular devices identical to those used for electrical measurements (17). By using this method, interrogation of silicon-monolayer-aluminum junctions have observed the presence of a new dielectric material, aluminum oxide, at the metal interface (2). The inclusion of another dielectric at the interface may alter the electrical response of the molecular junction and potentially give rise to hysteretic phenomena that have been previously attributed to molecular junctions (18). Three specific effects where chemistry dominates the resulting molecular electronic junction, linkage chemistry, metal interactions, and metallization will be highlighted in more detail.

Effect of Linkage Chemistry. Monolayers can be tethered to silicon under ambient conditions by using a variety of functional groups and reaction conditions. For simplicity, we will focus on the attachment of aliphatic chains with differing functional groups and thermal and UV reaction conditions. In the first case, we will consider reaction of alcohol, alkene, and thiol functional groups with silicon under thermal conditions. The S, O, and C atoms attach through a strong covalent bond giving rise to flow of partial charge from the silicon interface to the molecule (19). This can alter the electronic properties of the semiconductor by changing the band bending at the interface or by changing the polarization due to an induced dipole. More specifically, the work function of silicon can be altered by both band bending and dipole changes upon molecular bonding. Analysis of XPS and UPS data can distinguish between the relative contributions of these effects. In the case of aliphatic chains bonded to silicon through S, O, and C atoms, XPS data reveals the interfacial charge transfer differs for the n-type and p-type substrate doping but does not differ for the different Si-molecule linkage. UPS data indicates the work function for the Si-S and Si-C linked aliphatic chains are nearly identical while the work function for the Si-O aliphatic chains is  $\sim 0.2$  eV lower, indicating the oxygen interface is most electron rich. This work function difference arises from a dipole difference at the Si-O interface and indicates that a judicious choice of atomic linker can be used to electrically modify the silicon-molecule interface. Such molecular tethers can be used to engineer interfaces of conventional electronics to enhance current microelectronic scaling. By altering the atomic linkage of molecular layers, the work function of silicon can be altered and provide a buffer layer for subsequent growth of alternate materials, such as dielectrics or charge storage. In addition, molecular layers can be used to add functionality at the semiconductor-molecule interface for applications such as sensors of chemically sensitive field effect transistors. This has recently been realized with a molecularly controlled semiconductor resistor (20). Finally, molecular layers can be used as a gate-way for new electronic materials and devices that do not rely solely on silicon.

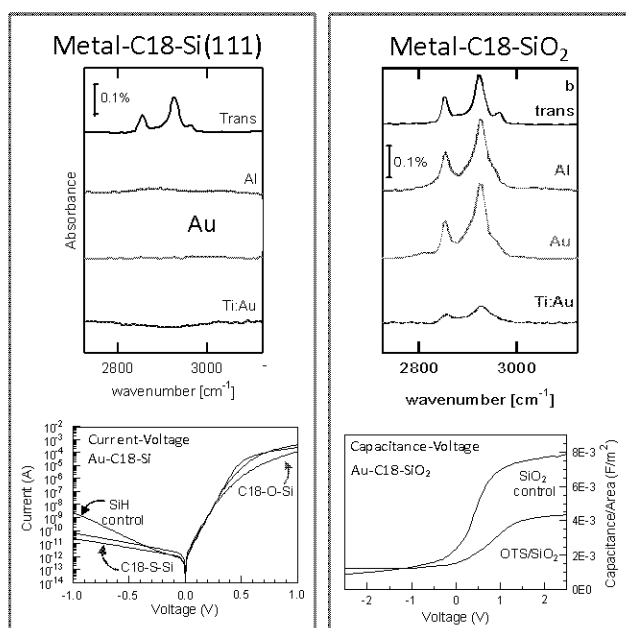
Effect of Metallization Conditions. As shown in Figure 2, the formation of top metal electrodes remains a challenge, often forming varied molecular junctions. Previous research has shown the metallization method can have a dramatic impact on the resulting physical structure and electrical properties. Identical aromatic molecular layers prepared from diazo starting materials were metallized by using either direct electron beam evaporation or a “soft” method where the sample is positioned within the evaporator with no direct path to the source. Metallization occurs while the evaporator is backfilled with a partial pressure of argon to increase scattering of gold atoms and decrease the energy of metal impinging on the molecular layer (21). Dramatic differences to the molecular layer were observed for these different experimental conditions and are shown in Figure 3. In the case of direct evaporation, there was no trace of the molecular layer following metallization. Instead, when soft metallization methods were used, p-polarized backside reflection absorption infrared spectroscopy (pb-RAIRS) data indicated that only traces of C-H fragments remained within the metal-silicon junction. Thorough cleaning of the input face confirmed these fragments were within the junction. In comparison, providing a “softer” means of metallization by relocating the sample and backfilling the chamber with argon results in preservation of the molecules as observed in the pb-RAIRS data. These results indicate the method used to apply the top metal electrode can have a dramatic impact on the resulting metal-molecule-semiconductor structure.



**Figure 3.** Metallization of molecular layers can result in a number of different products. The top shows direct metallization causes the monolayer to fragment leaving molecular residues on the surface. In the bottom case, evaporation is indirect with no line of sight to the source and the chamber contains a partial pressure of argon gas resulting in the preservation of the molecular layer as shown in the pb-RAIRS data.

Effect of Metal Interactions. Using the same metallization method on seemingly identical monolayers also produces very different results when those monolayers are prepared on different substrates. Previous studies compared metallization of aliphatic monolayers directly bonded to silicon with similar monolayers bonded to silicon oxide (3). After both samples were exposed to the same metallization conditions, the monolayers on silicon oxide were experimentally observed while the monolayers directly

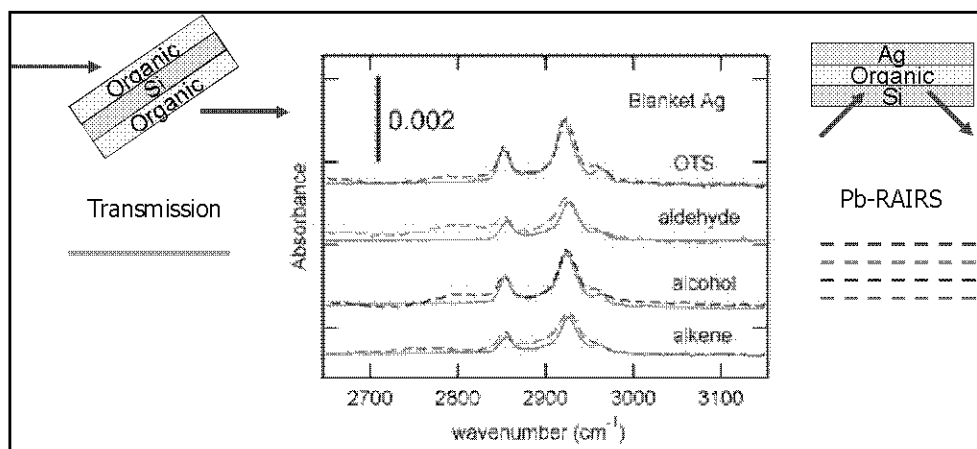
attached to silicon were no longer present in either the electrical or vibrational data as shown in Figure 4. One possible explanation for this differing reactivity may be due to the density of the monolayers. The molecules on silicon oxide are slightly denser than those directly attached to silicon as determined by spectroscopic ellipsometry and infrared spectroscopy. This lower packing density of the silicon-attached molecules could allow penetration of the metal within the molecular chains giving rise to shorting in the electrical measurements and screening within the vibrational spectra. Experiments performed on lower-density monolayers on silicon oxide, comparable to the silicon-based monolayers, still observed the molecules within the metal-silicon oxide junction indicating metal penetration is not the dominant mechanism responsible for the differing reactivity of monolayers on these two substrates. These findings highlight the previously ignored substrate-monolayer interfacial chemistry as playing a critical role in the interaction of organic monolayers and top electrodes.



**Figure 4.** Metallization of molecular layers on silicon and silicon oxide have different products. The molecules directly attached to silicon (left panel) are no longer evident after metallization in both pb-RAIRS and electrical measurements. However, molecules attached to silicon oxide (right panel) are still observed in the pb-RAIRS and electrical data under the top metal.

Follow-up experiments examined underlying mechanisms that may be responsible for differences in the metal reactivity of aliphatic monolayers on silicon and silicon oxide (22). The effect of linker chemistry was investigated as the silicon oxide molecules were attached through siloxane groups and the silicon-based monolayers were attached through covalent Si-O and Si-C linkers. It has been shown that Si-O interfacial bonds withdraw electron density from the silicon back bond thereby weakening the back bonds making them more susceptible to oxidation and potentially giving rise to the observed molecular desorption. The Si-C bonds do not suffer from this interfacial polarization and bond weakening. However, molecules tethered to H-Si(111) through Si-C bonds still were not observed after metallization (22). These findings suggest that the results are linked to the substrate-metal interaction which was confirmed by the study of silver evaporated onto

monolayers on the two substrate types. Depth profiling XPS data confirmed that within the Au junction, Au was actually mixing with silicon to form a silicide while Ag, a metal that does not readily form a silicide, remained on top of the molecular layer. Figure 5 presents pb-RAIRS data showing the molecular layer still visible under Ag. During metallization, the gold is able to diffuse through the molecular layer and react at the interface to form gold silicide and undercut the molecules. This process is suppressed when the silicon surface is passivated with an oxide or when the non-reactive silver metal is used. These results were somewhat surprising because prior to this, literature reports focused exclusively on interactions of the molecular layer with the top metal electrode, neglecting the substrate. Because monolayers on silicon form strong covalent bonds without self-assembling, there are likely many pinholes or other defects within the monolayer that facilitate the migration of metal to the interface. Due to the nanometer length scales and high energy of metallization, metal-substrate interactions are critical to consider when applying a top electrode on molecular electronic systems.



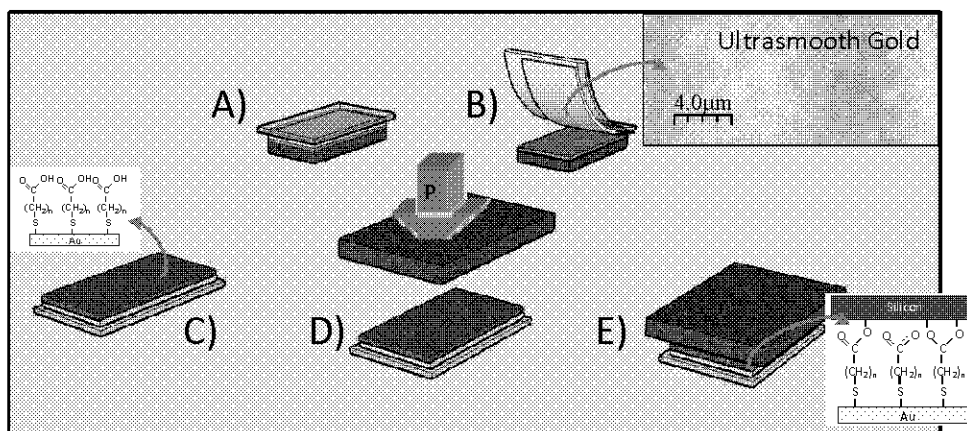
**Figure 5.** Reflection absorption infrared data of silver-molecule-silicon molecular junctions (dashed lines) and corresponding transmission spectra of samples prior to metallization. OTS is a C18 chain attached to silicon oxide. Aldehyde and alcohol refer to C18 molecules attached to Si through a Si-O linkage and alkene corresponds to a Si-C bonded C18 molecular layer.

### Novel Fabrication Approaches: Flip-Chip Lamination

There are many intrinsic properties to silicon-based molecular electronic structures that make reliable fabrication of junctions challenging. Although it is clear molecular layers on silicon impact the resulting electrical properties, making the metal-monolayer-silicon structure is challenging. First, because silicon is so reactive, controlling the surface bonding and achieving a dense, defect-free monolayer is a daunting task, especially for molecules with more than one functional group. Further, adding a metal contact to a monolayer remains a challenging process with deposition conditions and chemical interactions producing varied molecular electronic junctions. A novel solution is to flip the system around. Instead of evaporation of metal onto a monolayer, a well-ordered self-assembled monolayer (SAM) can be prepared on the



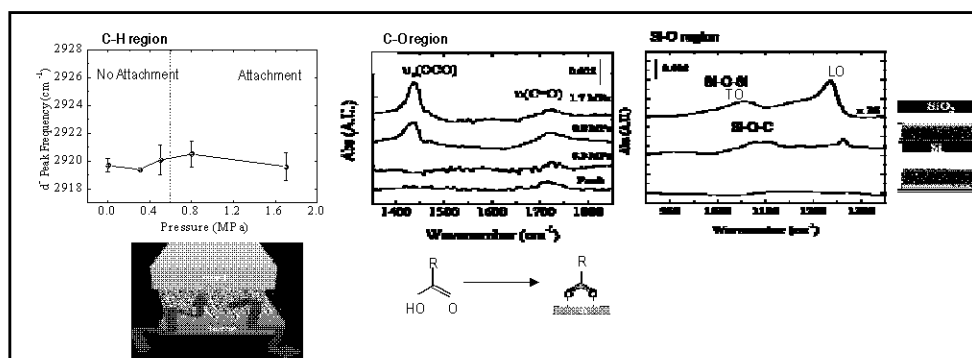
metal and subsequently be bonded to silicon. It is well known that thiols weakly adhere to the gold surface yet have a large enough surface mobility to align with their neighbors and self-assemble into dense films (23-25). Furthermore, gold is inert to many other functional groups enabling the production of high-quality monolayers composed of bifunctional molecules on gold surfaces. We can take advantage of these high quality monolayers and form reliable molecule electronic junctions by using a flip-chip lamination (FCL) approach as shown in Figure 6. In addition to dense bifunctional monolayers, this approach facilitates the use of ultrasmooth Au which is essential for many nano-electronic dimensions. The underside of the gold exhibits an root mean square (RMS) roughness of 0.5 nm while the top side of the gold surface, exhibits an RMS roughness of 2.5 nm (4). The FCL process begins with an ultrasmooth gold surface on a flexible polymeric substrate. This gold is produced by first evaporating gold onto a silicon oxide substrate previously treated with a fluorinated release layer. A flexible polymer (Polyethylene terephthalate, PET) is placed onto this metallic surface and moderate temperature and pressure are applied using a nanoimprint tool to facilitate bonding of the Au to the polymer and enable the Au to be peeled off revealing the ultrasmooth underside. Following SAM formation, the Au-molecular layer is flipped onto a H-Si(111) surface. Under mild conditions of pressure and temperature, the functional groups chemically bond with silicon. The flexible polymer backing on the preformed Au ensures conformal contact between the two surfaces and results in a robust metal-molecule-silicon electronic junction.



**Figure 6.** Flip chip lamination process. Gold is evaporated onto a substrate previously treated with a release layer and then lifted off to reveal the ultrasmooth underside (A and B). Monolayers are self-assembled on the gold surface (C) and brought into contact with H-terminated silicon surface under pressure and temperature (D) to form a chemical bond resulting in a semiconductor-molecule-metal junction (E).

Vibrational Characterization. The internal chemical and physical composition can be studied by using pb-RAIRS to identify changes in the molecular layer and changes in interfacial bonding. This technique allows for direct investigation of the structure of a buried molecular layer in samples that can also be used for electrical measurements. Figure 7 presents pb-RAIRS data that have been used to track the changes in molecular configuration and interfacial chemistry for FCL-fabricated metal-molecule-silicon structures. As the pressure increases between the metal and silicon surface, the junction

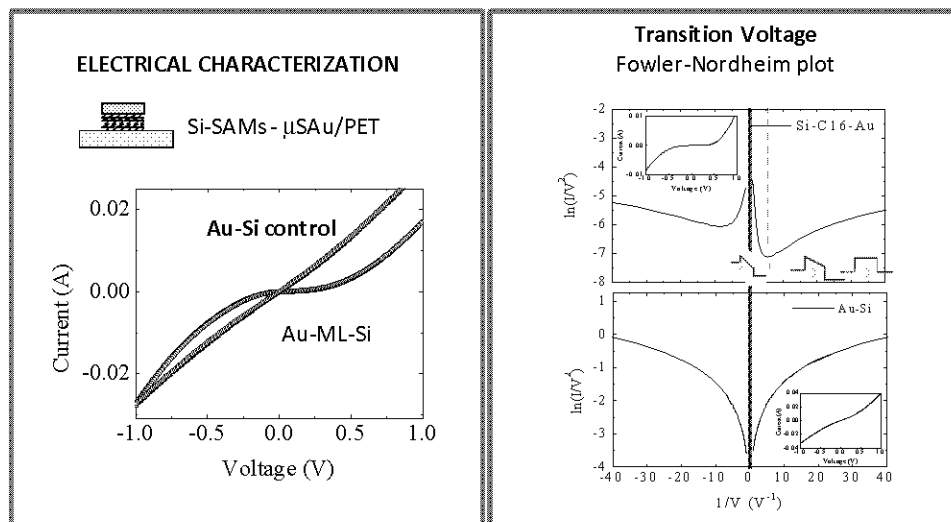
transitions from physically not adhering to being robustly chemically bonded. During this transition, the molecular chain orientation retains the same  $\nu$  C-H peak position, indicating the monolayer remains highly ordered. The C-O and Si-O spectral regions change with increasing pressure indicating bonding between the carboxyl groups and the H-terminated silicon surface (4). Evolution of this spectral region has been attributed to bonding of the oxygen atoms within the carboxyl group to the silicon surface through a symmetric bidentate coordination. The Si-O-C modes observed at  $1070\text{ cm}^{-1}$  and  $1105\text{ cm}^{-1}$  shown in Figure 7 further confirm this chemical interaction. Vibrational spectroscopy not only establishes the preservation of the molecular structure within the junction, it also shows the nature of the bonding between the molecules and the silicon substrate. Work with other molecular lengths found the nature of this carboxyl-silicon bonding changes in shorter methylene chain length molecules due primarily to differences in the original monolayer structure which alter the orientation and availability of the terminal functional group for bonding. Vibrational characterization provides important structural and chemical insight of the buried molecular layer to aid in the interpretation of the electrical data and provides knowledge to attribute proper charge transfer mechanisms.



**Figure 7.** pb-RAIRS vibrational spectra within the molecular junction as depicted on the lower left. Within the junction, the steady position of the C-H peak (left) indicates the molecular order is preserved while changes in the C-O (middle) and Si-O (right) spectral regions indicate chemical bonding between the carboxyl group and the silicon surface.

**Electrical Characterization.** Electrical characterization is more sensitive to defects and shorting than vibrational characterization. A small number of shorts between the two electrodes can serve as dominate charge transfer routes making the contributions from the molecular layer minimal to non-existent. Further, small changes in the effective dielectric thickness due to metal penetration which can shorten the dielectric or buckling and incomplete adhesion which can lengthen the dielectric have a dramatic impact on the measured capacitance and resulting electrical properties. Electrical measurements of patterned molecular junctions were performed to test the feasibility and reliability of flip-chip lamination for robust electrical device fabrication (4). Device areas  $(50 \times 50)\ \mu\text{m}^2$  were successfully flip-chip laminated with a transfer printing yield of 90%, as determined by optical microscopy. The electrical yield for the transferred devices was 100%. Figure 8 presents the current-voltage data obtained from FCL formed devices of C16 chains bonded to silicon and gold. The presence of the monolayer decreases the current compared to metal directly contacting silicon indicating the molecular layer is acting as a

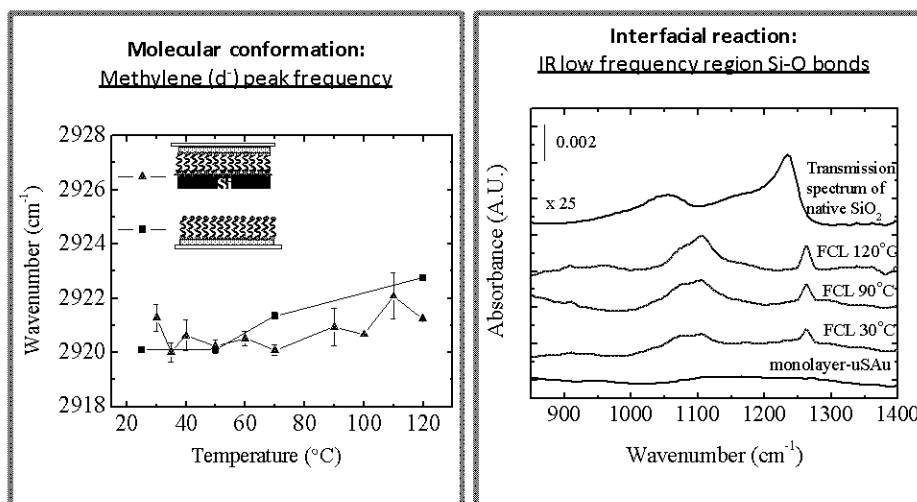
~2 nm ultrathin dielectric. The measured current density is comparable to other silicon-molecule-metal systems indicating the FCL approach forms molecular junctions free from electrical shorts. To facilitate quantitative comparison, the measured current density was transformed into a resistance per molecule. For the Au-C16-Si junctions, the resistance per molecule was determined to be  $6.7 \times 10^6 \text{ M}\Omega \pm 0.6 \times 10^6 \text{ M}\Omega$  in good agreement with previous values ( $10^4$  to  $10^6 \text{ M}\Omega$ )(15) of aliphatic molecules chemically bonded to both electrodes (4).



**Figure 8.** Electrical characterization of flip chip laminated molecular junctions. Current-voltage data (left) indicate the monolayer is acting as an ultrathin dielectric between the silicon and gold. Transition voltage spectroscopy (right) indicate the energy needed to transition from tunneling to field emission is  $\approx |0.2| \text{ V}$ .

Electrical data can also be used to extract charge transfer mechanisms and changes in transport from direct tunneling to field emission due to barrier height changes as a function of voltage. Transition voltage spectroscopy has been recently developed as a tool to experimentally measure the transition to Fowler-Nordheim tunneling and can be related to the band offsets in the molecular junction (26). Plotting the current voltage data in a Fowler-Nordheim plot ( $\ln(1/V^2)$  vs  $1/V$ ) shows a minima where this transition voltage occurs. At applied bias values less than the transition voltage, the barrier is essentially square and the charge is transported as direct tunneling through this barrier. At bias values above the minima in the Fowler-Nordheim plot, the voltage is sufficient to transform the barrier into a trapezoidal shape where field-emission becomes the dominate charge-transfer mechanism. The Fowler-Nordheim plot obtained from Si-C16-Au flip-chip laminated junctions is shown in Figure 8 with the transition voltage identified at  $\approx |0.2\text{V}|$  consistent with previously reported silicon-based molecule systems (27). The silicon-metal control is also shown with no observable bias consistent with a direct metal-semiconductor contact. Surprisingly, this transition voltage within the molecular system is located approximately one volt lower than comparable metal-molecule-metal junctions (28). This large difference between the metal-based systems and the semiconductor-based systems is likely due to the semiconductor interface and may be linked to transport facilitated by states at the semiconductor-molecule interface interface.

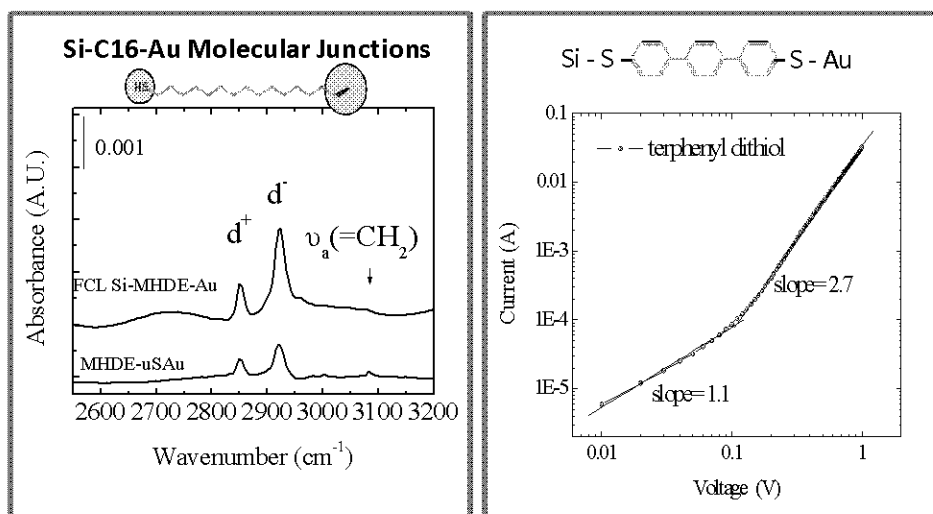
**Thermal Stability.** Many semiconductor fabrication processes either require the application of moderate to severe temperatures or samples are heated indirectly during processing. Elevated temperatures, however, may alter the chemical conformation and integrity of delicate components, such as organic monolayers. Elevated temperature can also be used in the flip-chip lamination process to drive differential adhesion and facilitate the transfer of materials from one substrate to another. Figure 9 presents pb-RAIRS data comparing the temperature response of the molecular layers confined within the junction to the response of free-standing SAMs exposed to the same thermal treatment (29). Thermal heating of the free-standing SAM causes a transition to higher wavenumber incorporating more *gauche* defects within the molecular chain. The monolayers buried within the metal-semiconductor contact show similar change with increasing temperature, indicating bonding of the molecule at both ends does not “pin” the chain to prevent disordering. Analysis of the Si-O spectral region, shown in Figure 9, as a function of temperature shows 1070  $\text{cm}^{-1}$  and 1107  $\text{cm}^{-1}$  Si-O-C features appear at low temperature, with minimal change in intensity or peak position, indicating the molecule-silicon reaction is not thermally driven. The molecular junction remains intact since there is no 1225  $\text{cm}^{-1}$  silicon oxide peak apparent despite the increased temperature. These findings demonstrate the formation of gold-monomer-silicon molecular junctions is achievable by FCL for temperatures up to 100  $^{\circ}\text{C}$ .



**Figure 9.** Temperature-dependent pb-RAIRS data of the molecular junctions. The left panel shows the preservation of the methylene peak position within the molecular junction and the right panel shows the evolution of molecule-silicon bonding as a function of applied temperature.

**Fabrication paradigm.** One of the advantages of the FCL technique is the thiol-based self-assembly allows for a variety of functional groups and molecules to be tested. In the case of aliphatic systems, we have explored the effect of molecular groups on the bonding efficiency to silicon. Both carboxyl and alkene groups bond to the H-terminated silicon surface during the flip-chip lamination process as shown in figure 10a. Further work is underway to understand the effect of temperature and pressure on the semiconductor bonding and resulting electrical properties (30). The effect of resistive aliphatic chains and conductive aromatic chains has been well studied for metal based molecular electronic systems. However, there is less directly comparable silicon-based

data due to the different chemistries typically needed to form the molecular layers. On silicon, aromatic monolayers are usually formed by reacting molecules with diazo functional groups while alkene, alcohol, thiol, and aldehyde functional groups typically attach to silicon under thermal or UV reaction conditions. The FCL technique allows formation of high-quality self-assembled monolayers on the metal surface first followed by direct bonding to silicon. Figure 10 shows aromatic molecules bonded through thiol linkers to both Au and Si electrodes and prove to be free from metallic shorts. The current-voltage plot shows two transport regions with a slope of 1.1 and 2.7 consistent with previous results of metal-aromatic monolayer-metal junctions (31). Electrical measurements of molecular junctions formed by using FCL allows direct comparison of aliphatic and aromatic species, in addition to, probing the effect of semiconductor and metallic electrodes furthering the research and development of nanoscale molecular layers.



**Figure 10.** FCL extended to other molecular functional groups. Bonding of carboxyl groups and alkene groups to silicon has been achieved. (left panel) The right panel shows aromatic molecules bonded through thiol linkers prove to be free from metallic shorts.

The flip-chip lamination process has many advantages over the previous direct and soft metallization routes. Metal is lifted onto a PET substrate revealing the ultrasmooth underside which is important for many nanoelectronic applications. In addition, the metal can be first evaporated through a shadow-mask or otherwise patterned prior to transfer to the PET substrate, allowing the formation of electrical junctions that do not need additional processing. This is advantageous for many sensitive materials, including organic and biological molecules, which degrade and alter conformation with processing conditions. Additionally, this is a clean process that does not introduce photoresist or materials that may alter electrical properties if not fully removed. As such, this process is transferrable to a number of electrical technologies relying on alternate materials and experiments are underway to use flip-chip lamination to create organic crystalline field effect transistors and other nanoelectronic devices.

## Conclusions

We have presented the measurement science and technology behind silicon-based molecular electronic junctions. The silicon surface is quite reactive, making attachment via direct functionalization challenging, but accessible through a variety of reaction conditions. Application of the top metal electrode remains one of the dominate failure mechanisms for fabrication of these nanoelectronic devices. It has been shown that alternate metallization procedures for forming the top electrode produce devices retaining molecular integrity. Metallization of monolayers directly attached to silicon presents an additional consideration-the interaction of the metal with the silicon substrate. While there are a number of interesting routes to deal with the intrinsic properties that limit reliable fabrication of molecular electronic devices, the most promising fabrication route appears to be flip-chip lamination. This FCL process uses two preformed electrodes which are ultrasoft and forms a bifunctional monolayer on the electrode that forms the best SAM. Next, the two electrodes are laminated together, linked with chemical bonding of the monolayer to each surface. This process offers many advantages over the step-wise bottom-up approach that is typically used for molecular electronic junction fabrication and can be directly applicable to many other technologies.

In order to create optimal junctions, it is important to take into account the interaction of all species present in the molecular electronic junction. Understanding these interactions leads to innovative means of creating nanoelectronic systems that can enable the manufacturing, innovation, and invention of new technologies.

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