Thermal stability of confined flip-chip laminated ω-functionalized monolayers

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The authors present the results of an IR study of the effect of temperature on the formation of Au-monolayer-Si molecular junctions by using a flip-chip lamination approach. Carboxylic acid-terminated alkanethiols self-assembled on an ultrasmooth gold substrate have been laminated to H–Si(111) at 0.8 MPa as a function of temperature. *p*-polarized-back-side reflection absorption infrared spectroscopy of the alkanoic acids within the molecular junction indicates increasing disorder, likely near the carboxylic acid (–COOH) terminus, of the all-*trans* chain up to 60 °C, followed by a propagation of these defects down the molecular length. The low frequency region of the IR spectra as a function of temperature indicates that the –COOH group is interacting with the H–Si(111) surface. The IR spectra indicate that the reaction is largely due to the availability of the COOH groups to react. Flip-chip lamination is an effective approach to form molecular junctions. Unlike direct metal evaporation, it ensures the formation of robust structures where the organic monolayer is chemically bonded to both surfaces with no signs of metal penetration. © *2009 American Vacuum Society.* [DOI: 10.1116/1.3259934]

I. INTRODUCTION

Self-assembled monolayers confined between two solid surfaces are of particular interest in a wide range of technological applications from lubrication to molecular electronics. In particular, the formation of Au-monolayer-Si structures has attracted much attention because they hold great potential for next generation memory and logic devices. However, the formation of densely packed monolayers on silicon and their connection to the metal electrode remain one of the most important challenges for the fabrication of reliable molecular electronic devices. Direct evaporation of the metal on the organic material results in low yields of functional devices because the metal tends to electrically short through the molecular monolayer and can even displace the molecules directly attached to silicon.[1] Soft-metallization approaches such as Hg drop,[2] indirect metal evaporation,[3] or nanotransfer printing (nTP)[4,5] have been reported as promising alternatives. The versatility of nTP to contact self-assembled monolayers (SAMs) with metal has been previously demonstrated exploiting the strong chemical interactions between thiols and Au surfaces.[6] However, metal surface roughness of above 2 nm generates small gaps between the metal and organic monolayer which results in a decreased contact area leading to unreliable electrical results. Ultrasmooth metal surfaces combined with bifunctional SAMs are paramount factors to control the interlayer adhesion and ensure conformal contact to molecules. Pressure

and temperature can enhance interfacial adhesion,[7] but these conditions might modify the molecular conformation and interfacial bonding within the molecular junction. The molecule-electrode interface not only establishes a chemical bond to ensure stable and reliable devices but also can dominate charge transport across molecular junctions. In addition, there is a strong correlation between the molecular configuration and the electronic properties of the molecular junction, making it essential to carefully assess buried monolayer film structure and interfacial interactions.[8,9]

Monolayers often encounter increased temperatures during processing or use. For example, patterning, etching, and metallization steps often include thermal cycles up to 100 °C. Monolayers utilized for antifriction coatings or electronic applications can be exposed to more intense local heating that can irreversibly alter the molecular layer. Previous temperature studies of SAMs have reported two main thermal-induced degradations; conformational defects followed by desorption or decomposition.[10–12] Typically, it was observed that changes in aliphatic chains at low temperatures begin with reversible gauche defects located near the chain end. Above ≈80 °C, these defects are able to diffuse to the middle of the molecule due to a more vertical chain orientation leading to irreversible molecular entanglement. Above ≈130 °C, desorption becomes a dominate contribution as indicated by infrared spectroscopy, scanning tunneling microscopy, x-ray photoelectron spectroscopy and contact angle measurements.[10,13] While these temperature-induced changes are well documented for SAMs, the temperature-

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induced changes for a molecular film confined between two solid surfaces have not been fully investigated.

Previously we have examined pressure-induced changes in the molecular film confined within a junction fabricated with flip-chip lamination (FCL). By first forming monolayers on ultrasmooth Au, we were able to utilize the self-assembly of thiol groups to create a dense monolayer of ω-functionalized molecules, which is quite challenging on silicon. The molecular junction is then formed by bringing the monolayer-Au surface in contact with a H-terminated Si(111) surface with applied temperature and pressure.[14] This earlier work reported both vibrational and electrical data indicating that electrical contact to the monolayer is formed while preserving the integrity of the molecules without metal filaments. The pressure-induced FCL approach provides a facile means to fabricate high-quality molecular junctions consisting of dense monolayers chemically bonded to metal and silicon electrodes. However, a detailed understanding of the factors influencing the interfacial COOH–Si interaction is not well understood. Exploration of the molecular structure and interfacial reaction as a function of temperature can help to realize the factors influencing adhesion.

In the work reported here, we (1) compare the temperature response of the molecular layers confined within the junction to the response of freestanding SAMs exposed to the same thermal treatment, (2) evaluate the temperature-induced reaction between the COOH-terminated SAMs and the H–Si surface, and (3) contrast the structure of the temperature-induced molecular junction with our previously reported pressure-induced molecular junctions. In this work we use the nTP to obtain ultrasmooth gold films (uSAu) on plastic substrates followed by self-assembly of bifunctional molecules to form dense Au-thiol monolayers. In particular, we have investigated mercaptohexadecanoic acid (MHA) and mercaptoundecanoic acid (MUA) self-assembled monolayers (SAMs) which contain a –COOH terminal group capable of bonding to the H–Si (111) substrate.[14] This FCL approach facilitates the formation of reliable metal-molecule-Si junctions preserving the integrity of the molecules.

II. EXPERIMENT

Materials and sample preparation. The substrates used in the present study are ultrasmooth gold on polyethylene terephthalate (PET) fabricated by direct evaporation of 200 nm of gold on Si substrates previously treated with a release layer.[7] The silicon substrates were double-side polished Si (111) float zone wafers (*n*-doped, 3000–5800 Ω cm). H-terminated silicon substrates were prepared by immersion into a cleanroom grade buffered oxide 6:1 etch (NH_4F:HF), rinsed with 18 MΩ cm water and dried with nitrogen.

Monolayer formation. All chemicals were purchased from Sigma-Aldrich[15] (11-mercaptoundecanoic acid 95%, MUA; 16-mercaptohexadecanoic acid 99%, MHA) and used as received. Au substrates on PET were cut into approximately 1×1 cm^2 squares and placed for 5 min in an ultraviolet

(UV)/ozone cleaner, rinsed with water and ethanol, dried with N_2 gas, and returned to the UV/ozone cleaner for 10 min. Then substrates were rinsed with ethanol and dried with N_2 gas before being immersed in 1×10^{-3} mol/l alkanethiol solution overnight. The resulting samples were rinsed with 2 mol/l HCl acid at 65 °C to eliminate adsorbates and promote protonated carboxylic acid termination. The Au-SAM-Si structures were fabricated by FCL.[14] Briefly, a freshly terminated H–Si(111) substrate was placed in contact with the SAMs-uSAu/PET and pressed at 0.8 MPa for 5 min while applying a temperature ranging from 30 to 120 °C. Intimate contact between H-Si(111) and SAM-uSAu/PET was achieved for the entire temperature range as evidenced by adhesion of the two substrates upon removal from the imprint tool.

Monolayer characterization. Self-assembled monolayers are characterized prior to formation of the sandwich structure by reflection absorption infrared spectroscopy (RAIRS) recorded by using a commercial Fourier transform instrument with a liquid nitrogen cooled mercury cadmium telluride detector (600–4000 cm^{-1}) set to 8 cm^{-1} resolution. The angle of incidence was 69° from the surface normal. Spectra of these bare SAMs on uSAu/PET were referenced to evaporated gold on silicon (Au/Si). Following formation of the ultrasmooth metal-molecule-silicon structure, *p*-polarized back-side reflection absorption infrared spectroscopy (pb-RAIRS) has been used to characterize molecular structure and chemical bonds of these confined monolayers. The Si-SAM-uSAu structures were referenced to evaporated gold on double-side polished H–Si(111). The incident beam is transmitted through the silicon substrate and reflected from the Au surface which facilitates the characterization of the sample *in situ* at the buried junction. FCL samples and reference have been backside treated under UV/ozone to minimize the contribution of contaminants from the outer surface of silicon substrate.

III. RESULTS AND DISCUSSION

The thermal behavior of the monolayers confined within the molecular junction has been compared to freestanding monolayers of MHA and MUA on uSAu/PET which were exposed to the same temperature range, from 30 to 120 °C, for 5 min on a hot plate. In both architectures, fresh samples have been used for each temperature test to minimize effects from thermal cycling. Vibrational spectra were acquired at ambient conditions after the thermal-treated samples reached equilibrium.

Figure 1 shows the C–H IR spectra of MHA monolayers (a) on uSAu/PET and (b) within the Si-MHA-uSAu laminated structure prepared by using 0.8 MPa and ≈30 °C. The symmetric (d^+) methylene stretch at 2850 cm^{-1} and the asymmetric (d^-) methylene stretch at 2919 cm^{-1} are observed. These frequencies indicate the well-ordered all-*trans* zig-zag structure of the monolayer is preserved within the molecular junction after lamination.[16,17] This is not unexpected since it has been reported that higher temperatures (above 80 °C) and pressures (above 800 MPa) are necessary
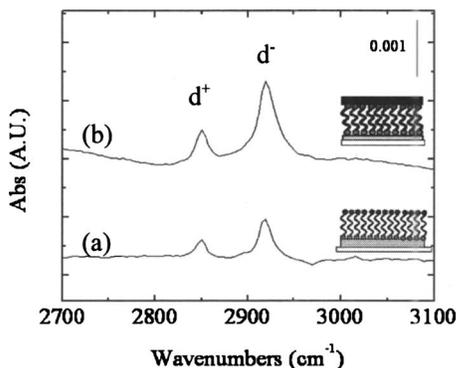
FIG. 1. Vibrational spectra of (a) freestanding MHA-uSAu/PET and (b) flip-chip laminated Si–MHA–uSAu/PET at 0.8 MPa and 30 °C.

to irreversibly degrade the monolayer quality.[11,18–21]

The spectra were obtained at room temperature after thermal exposure making them sensitive to irreversible changes in the molecular junction. The CH_2 asymmetric peak frequency, FWHM, and integrated absorbance intensity are shown as a function of temperature in Fig. 2 for freestanding MHA on ultrasmooth gold and within the molecular junction.
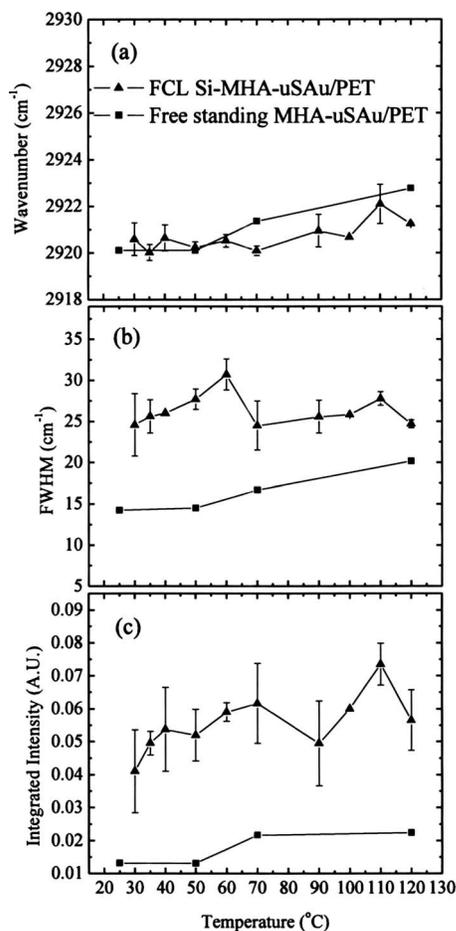

FIG. 2. Temperature dependence of (a) peak frequency, (b) FWHM, and (c) integrated intensity for the antisymmetric stretching mode (d^-) of flip-chip laminated Si-MHA-uSAu/PET structures (▲) and MHA-uSAu/PET (■) freestanding monolayer control.

For the freestanding MHA-uSAu/PET, with increasing temperature the peak frequency and FWHM increase, indicating a transition to less-ordered molecular layers. The integrated intensity has a transition around 60 °C where the increased intensity is likely due to the increased conformational disorder. This is consistent with the gradual and irreversible disordering of the monolayers due to the incorporation of gauche defects at the end of the alkyl chain, commonly observed in n-alkane monolayers.[10] For the FCL molecular junction, the methylene (d^-) peak frequency varies within 2 cm^{-1} as a function of temperature indicating solidlike structure is preserved. The FWHM slightly increases initially, maximizes at the 60 °C transition temperature, decreases, and remains constant. This may be due to the increased gauche heterogeneity up to the transition temperature while the chains retain an overall all-*trans* conformation as seen by the ≈2921 cm^{-1} peak position. Above this transition, the spectra have a near constant FWHM which indicates there are no additional conformational defects. The integrated intensity as shown in Fig. 2(c) is larger for the FCL molecular junctions which is likely due to a change in orientation of the molecular group. Because of the metal surface selection rule, changes in tilt have a large contribution on the methylene intensity. However, since the peak frequency remained at typical values for the solidlike methylene structure, the monolayers are still highly ordered. We cannot rule out contributions from organic contaminants, but expect these to be minimal. This intensity divergence already appears at ambient conditions which probably indicate that it is due to a pressure-induced change rather than a thermal effect. Overall molecules confined within a molecular junction have a somewhat similar response to applied temperature when compared to freestanding SAMs.

The spectra of the shorter chain MUA monolayers on uSAu/PET after lamination, within the molecular junction, exhibit a very similar behavior (data not shown). The MUA-uSAu/PET monolayer structures before lamination commonly show values of (d^-) peak frequency around 2923 cm^{-1}, indicating less ordered monolayers, as expected from the reduction in van der Waals forces due to the shorter alkyl chain.[17,22] After lamination, the asymmetric methylene peak frequency is at ≈2921 cm^{-1} for the entire temperature range. Therefore, it appears that FCL induces more order in the short chain monolayers similar to previous results of pressure annealing[14,19,21] and adheres the monolayers to the silicon substrate while preserving an all-*trans* configuration up to 100 °C.

Previous studies of the temperature dependence of similar bare monolayers reported two different phase regimes as a function of temperature.[20,23,24] As the temperature initially increased, the molecular chains became more disordered and tilted toward the surface normal and were reflected in the IR spectra by a decrease in integrated intensity. The conformational gauche defects were identified by an increase in the integrated intensity, FWHM, and peak position. At higher temperatures, desorption and/or decomposition are evidenced by a decrease in the intensity of the infrared spectra.
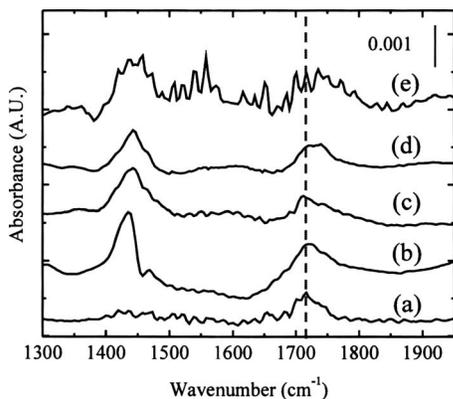
FIG. 3. Vibrational spectra of the C–O region of (a) the freestanding monolayer MHA-uSAu/PET sample and the flip-chip laminated Si-MHA-uSAu/PET molecular junction formed by using 0.8 MPa and (b) 30 °C, (c) 50 °C, (d) 90 °C, and (e) 120 °C.
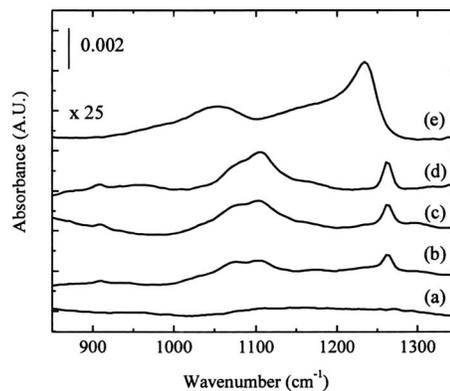

FIG. 4. Vibrational spectra of the Si–O region of (a) freestanding MHA-uSAu/PET monolayer and the flip-chip laminated Si-MHA-uSAu/PET molecular junctions formed at 0.8 MPa and (b) 30 °C, (c) 90 °C, and (d) 120 °C. Brewster's angle transmission spectrum of native oxide silicon (e).

Thus, the spectra of the MHA and MUA monolayers within the molecular junction indicate increasing disorder, likely near the COOH terminus, of the all-*trans* chain up to 60 °C followed by propagation of these defects further down the molecular length weakening the van der Waals interchain interactions and increasing the peak frequency. The temperature-induced defects near the COOH terminus may have an effect on the adhesion ability by altering the acid orientation and reactivity. Also, no desorption was observed within the FCL molecular junction. Thus, compared to previous studies on the thermal stability of SAMs where the alkyl chain evolves to liquidlike structure and onset desorption temperature was reported above 100 °C,[10,23] the monolayers studied here are much less degraded. These differences are likely due to experimental differences in sample thermal cycling.[10,23]

Chemical modification at the COOH–Si interface has been determined at the different lamination temperatures from the pb-RAIRS spectra of the C–O and Si–O regions. Figure 3 shows evolution of the IR C–O region (1300–1900 cm^{-1}) for uSAu-MHA-Si molecular junctions exposed to 30, 50, 90, and 120 °C and compared with a freestanding MHA-uSAu/PET monolayer. Before lamination, the MHA monolayer spectrum contains a peak at 1720 cm^{-1} attributed to the H-bonded carbonyl group in COOH, commonly observed in alkanoic SAMs.[24,25] After lamination, the carbonyl peak at 1721 cm^{-1} persists and a new shoulder appears near 1740 cm^{-1} which is consistent with an ester, perhaps due to a Si–O–(C=O)–R species.[25] In addition, a low-frequency peak at $\approx$1440 cm^{-1} is observed which is assigned to a symmetric carboxylate stretching mode, $v_s(OCO)$.[24,25] The observance of the symmetric vibration and not the asymmetric vibrational mode suggests the OCO group is oriented in a bidentatelike coordination with the two oxygen atoms interacting symmetrically with the semiconductor.[14,26,27] In the 30 °C spectrum shown in Fig. 3(b), a small contribution at 1465 cm^{-1} attributed to CH$_2$ scissor deformation is observed.[24,25] With increasing

lamination temperature, the peak at $\approx$1440 cm^{-1} broadens considerably which is probably due to a more heterogeneous environment as the *gauche* defects become incorporated and perhaps incorporation of the CH$_2$ scissor deformation. Therefore, it is suggested that the contribution of CH$_2$ deformation modes overlaps the carboxylate peak in IR spectra. The 120 °C spectrum [Fig. 3(e)] contains significant background noise suggestive of a strong contribution of water which may be due to side reactions or H$_2$O incorporation within the molecular junction during the lamination process.

Further analysis of the COOH/Si interaction is obtained from evaluation of the Si–O spectral region (700–1300 cm^{-1}), as shown in Fig. 4. The spectrum of the monolayer prior to lamination [Fig. 4(a)] contains no observable peaks in this region while the spectra of the Si-MHA-uSAu/PET FCL molecular junctions [Figs. 4(b)–4(d)] exhibit a broad band at $\approx$1100 cm^{-1} and a sharp peak at 1263 cm^{-1}. The broad band was fitted to two components at 1070 and 1107 cm^{-1} assigned to Si–O–C modes.[14,28] The Brewster's angle transmission spectrum [Fig. 4(e)] of native SiO$_2$ (typically 1.2 nm) contains a TO oxide phonon at 1061 cm^{-1} and a LO oxide phonon at 1226 cm^{-1}. The absence of the peak at 1226 cm^{-1} in the molecular junction spectra indicates that minimal oxidation takes place during lamination. The Si–O–C mode confirms chemical interaction between –COOH groups and H–Si surface consistent with the observation of the esterlike peak in the C–O spectral region. The peak at 1263 cm^{-1} is probably due to a Si–O–C stretch[14,28] but may have contributions from C–O–C or C–O–H species which also appear in this spectral region.[24,25] The peak positions and area of these modes do not change significantly when the lamination temperature increases consistent with the C–H and C–O spectra. These data suggest the extent of reaction between the COOH-terminated monolayers and the H–Si substrate is not temperature dependent.

Figure 5 shows the C–O vibration spectra for MUA monolayers laminated at 30, 90, and 100 °C. Previous detailed studies of the MUA molecular junctions laminated at 30 °C reported four contributions assigned to $v(C=O)$ at
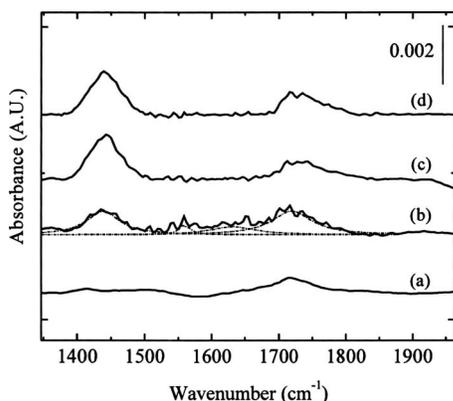
FIG. 5. Vibrational spectra of the C–O region of (a) freestanding MUA-uSAu/PET monolayer and the flip-chip laminated Si-MUA-uSAu/PET molecular junction prepared at 0.8 MPa and (b) 30 °C, (c) 90 °C, and (d) 100 °C.

1720 cm^{-1}, υ(OCO) at 1445 cm^{-1}, and υ_{as}(OCO) at 1558 and 1627 cm^{-1}, indicating that the carboxylic acid groups interact asymmetrically with silicon.[14] In contrast, the spectra of the molecular junctions created with increasing temperature contain only the υ(OCO) contribution with increasing intensity while the υ_{as}(OCO) contribution disappears, suggesting a bidentate coordination mode with the two oxygens interacting symmetrically. As we previously mentioned for FCL MHA SAMs, we do not rule out the contribution of CH$_2$ deformation modes in the peak assigned to υ(OCO). The Si–O IR spectra, shown in Fig. 6, contain the Si–O–C band which supports chemical bond formation between Si and –COOH, similar to the behavior observed for MHA samples. The MUA samples laminated at 120 °C did not adhere to the Si substrate after removal from the nanoimprint tool. The adhesion of the MHA monolayers under similar conditions indicates that this lack of adhesion of the MUA samples is linked to the monolayer itself. The less dense MUA monolayer contains more defects initially and less
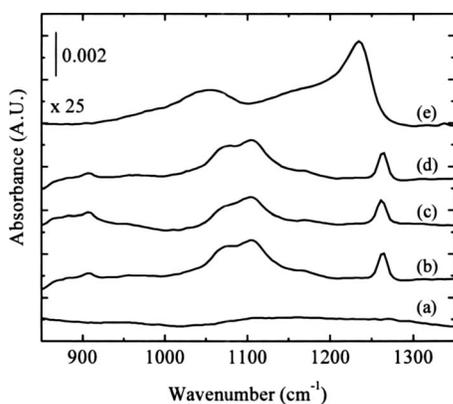

FIG. 6. Vibrational spectra of the Si–O region of (a) freestanding MUA-uSAu/PET monolayer and the flip-chip laminated Si-MUA-uSAu/PET molecular junction prepared at 0.8 MPa and (b) 30 °C, (c) 90 °C, and (d) 100 °C. Brewster's angle transmission spectrum of native oxide silicon (e).

steric hinderance to chain reorientation; thus chemical and/or physical changes at the –COOH group are likely hindering lamination.

The behavior of the organic monolayers laminated while applying temperature is in contrast to our previous results of pressure-induced lamination at room temperature. Different bonding environments were observed for the junctions formed at low pressure which is likely converted to a bidentatelike configuration at higher pressure. Also, as the pressure increased the extend of interfacial reaction between –COOH monolayer terminus and H–Si (111) surface increased.[14] In the case when temperature is applied during lamination, the extent of reaction does not increase at higher temperature. When the temperature increases to 120 °C, the dense MHA monolayers still adhere to the silicon substrate since steric constraints limit the orientation of the acid group; however, the less-dense MUA monolayers do not adhere since the chains have become sufficiently disordered to remove a substantial amount of COOH groups from the reactive Si–H surface. The observations of no adhesion at higher temperatures for MUA monolayers and the observance of nearly identical spectra in the Si–O and C–O region with increasing temperature indicate that bonding is limited by the proximity of the acid groups to the Si substrate.

IV. CONCLUSIONS

We have demonstrated that the formation of Au-monolayer-Si molecular junctions is achievable by FCL for temperatures up to 100 °C. Molecules confined within a molecular junction have a somewhat similar response to applied temperature when compared to freestanding SAMs. The incorporation of gauche defects occurs near the same transition temperature for both systems. In addition, the *gauche* defects appear near the chain terminus, which indicates that the interaction between the COOH–Si is not strong enough to prevent the aliphatic groups from disordering. Moreover, the interaction may be driven largely by kinetics rather than thermodynamics as increasing thermal energy actually weakens adhesion while increasing pressure appears to strengthen adhesion. The FCL approach allows the formation of molecular junctions utilizing a broad range of temperatures and pressures during fabrication to achieve high-quality monolayers chemically bonded to both electrodes while minimizing contributions from metal filaments. Our FCL approach can be utilized to further explore the role of molecular conformation and monolayer-electrode interface on the electronic transport within molecular junctions.

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