

## FTIR Spectroscopy of Buried Interfaces in Molecular Junctions

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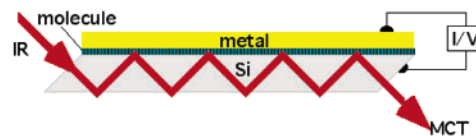
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Charge transport across nanoscopic molecular junctions based on single or a small group of molecules has attracted great attention in the last a few years.<sup>1,2</sup> In most experiments reported to date, the critical charge-transporting interfaces are *buried interfaces* which are not readily accessible to conventional structural or spectroscopic probes. The difficulty in verifying and determining molecular structure and conformation at buried interfaces has produced a critical knowledge gap responsible for the confusion and controversy regarding the mechanism for observed *I/V* characteristics.<sup>3–6</sup> In some cases, one must face the reality that claims of molecular switches,<sup>7,8</sup> although attractive, should likely be dismissed.<sup>9,10</sup>

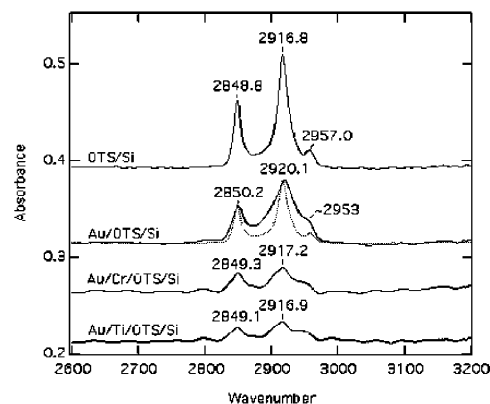
Perhaps the most attractive method for structural and conformational analysis of molecules at interfaces is vibrational spectroscopy. Two groups reported recently the application of reflection–absorption Fourier transform infrared (RA-FTIR) spectroscopy to investigate the deposition of metal atoms on thiolate self-assembled monolayer (SAM)-covered Au surfaces.<sup>11,12</sup> These studies provided great insight into the penetration and chemical interaction of metal atoms with SAMs but are restricted to the initial stage of metal deposition due to the high IR absorbance in metals. Inelastic electron tunneling spectroscopy (IETS) can probe a true buried interface, as shown most recently for metal–SAM–metal junctions by Wang et al.<sup>13</sup> and Kushmerick et al.<sup>14</sup> Potential limitations of IETS include poor spectral resolution, low temperature requirement, and the unavoidable coupling of spectroscopic measurement to transport. Here, we present an alternative method generally applicable to the recording of high-quality FTIR spectra of buried interfaces in molecular junctions. This is based on attenuated total internal reflection (ATR) FTIR spectroscopy and molecular junctions fabricated on semiconductor (e.g., Si, Ge, GaAs) substrates, Figure 1. Here, the IR-transparent semiconductor substrate not only makes ATR-FTIR possible but also serves (when doped or covered with a thin metal film) as an electrode.

To demonstrate the methodology, we use two well-established systems: octadecyltrichlorosilane (OTS) self-assembled monolayer (SAM)<sup>15,16</sup> on native oxide-terminated Si and mercaptohexadecanoic acid (MHA) multilayers<sup>17</sup> on thin Au film-covered Si. The samples were Si(111) parallelogram plates designed for multiple internal reflection spectroscopy ( $50 \times 10 \times 1 \text{ mm}^3$ , 50 reflections). To prepare high-quality OTS SAMs on Si, we adopted a procedure similar to that of Sagiv and co-workers.<sup>18</sup> For MHA self-assembly multilayers, we adopted the procedure of Ulman and co-workers.<sup>17</sup> The Au surface was prepared by the deposition of 30 Å of Au onto H-terminated Si(111) in a vacuum evaporator. For the top contact, Au was deposited either without or with an 80 Å Cr or Ti adhesion layer on both sides of each OTS SAM or MHA multilayer-covered Si sample at a deposition rate of 1 Å/s. The total thickness of the metal film was 800 Å in each case. All spectra presented in this report were recorded without the application of bias voltage as illustrated in Figure 1.

Figure 2 shows the C–H stretch region of FTIR spectra for OTS SAM on silicon before and after metal deposition. Without metal deposition, the OTS/Si spectrum is characterized by three peaks: the symmetric ( $\nu_s = 2848.8 \pm 0.5 \text{ cm}^{-1}$ ) and asymmetric ( $\nu_a =$

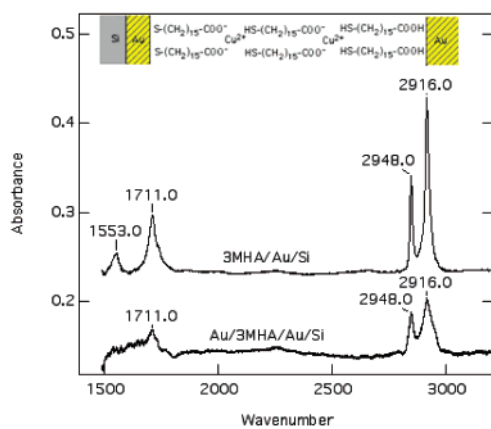


**Figure 1.** (Not to scale) ATR-FTIR of the buried interface at a metal–molecule–silicon tunnel junction. MCT: liquid nitrogen cooled mercury–cadmium–telluride detector.



**Figure 2.** ATR-FTIR spectra of OTS SAM on Si with or without the deposition of 800 Å metal overlayers. The OTS/Si spectrum is also scaled and reproduced as the dotted curve.

$2916.8 \pm 0.5 \text{ cm}^{-1}$ ) stretching modes of  $\text{CH}_2$ , and a weak contribution at  $2957.0 \pm 0.5 \text{ cm}^{-1}$  from the asymmetric stretch in terminal  $\text{CH}_3$  groups. The symmetric  $\text{CH}_3$  stretching mode is not resolved. This spectrum, particularly the  $\nu_a$  ( $\text{CH}_2$ ) frequency, is characteristic of a close-packed, well-ordered SAM with alkyl chains in all-trans configuration.<sup>16,18</sup> After the deposition of 800 Å Au on the SAM, the FTIR spectrum shows little change in peak area, but small shifts in peak positions (2–3  $\text{cm}^{-1}$  for the symmetric and asymmetric stretches of  $\text{CH}_2$ ). Upward shifts in  $\nu_s$  and  $\nu_a$  frequencies of  $\text{CH}_2$  are usually associated with the introduction of conformational disorder in the alkyl chains.<sup>11,16</sup> More dramatic changes are seen in peak width: the fwhm of the  $\nu_a$  ( $\text{CH}_2$ ) peak increases from 19  $\text{cm}^{-1}$  for OTS/Si to 46  $\text{cm}^{-1}$  after Au deposition. The dotted curve in Figure 2 is a scaled reproduction of the FTIR spectrum of the OTS SAM. This comparison clearly reveals that, upon Au deposition, the  $\nu_a$  ( $\text{CH}_2$ ) peak shifts in both directions, leading to a total broadening of 240%. A similar observation can be made for the  $\nu_s$  ( $\text{CH}_2$ ) peak. An upward shift in the  $\text{CH}_2$  stretch frequencies is usually interpreted as increased gauche defect density within the monolayer of alkyl chains.<sup>11,16,18</sup> On the other hand, the downward shift in the  $\text{CH}_2$  stretch frequencies is indicative of *direct* interaction of  $\text{CH}_2$  groups of the alkyl chain with metal atoms. Although the  $\nu_a$  ( $\text{CH}_3$ ) peak is not well resolved after Au deposition, there is also clearly a downward shift in peak position. This kind of softening of C–H stretch vibrations is well-known for the adsorption of alkanes on a variety of metal surfaces.<sup>19</sup> Typical decreases in C–H stretch vibrations of up to 20  $\text{cm}^{-1}$  are commonly observed and are interpreted as due to the presence of C–H...metal bonding. This observation suggests that the deposition of Au on the SAM surface results in not only conformational disorder but also the direct contact between the deposited metal and the alkyl backbones. This



**Figure 3.** ATR-FTIR spectra of MHA trilayer on 30 Å Au/Si before (upper) and after (lower) the deposition of 800 Å top Au contact.

**Table 1.** FTIR Data for OTS/Si without and with Metal Deposition

	$\nu_a$ (cm <sup>-1</sup> )	$\nu_s$ (cm <sup>-1</sup> )	fwhm, $\nu_a$ (cm <sup>-1</sup> )	peak area
OTS/Si	2916.8 ± 0.5	2848.9 ± 0.5	19	1.0
Au/OTS/Si	2920.1 ± 0.5	2850.2 ± 0.5	46	1.0
Au/Cr/OTS/Si	2917.2 ± 0.5	2849.3 ± 0.5	~31	0.4
Au/Ti/OTS/Si	2916.9 ± 0.5	2849.1 ± 0.5	~30	0.3

is in agreement with previous conclusions that Au atoms penetrate the molecular films when they are deposited onto alkanethiolate SAM-covered Au surfaces.<sup>11,12,20</sup> Note that in the work of Walker et al.,<sup>12</sup> softening of C–H stretch vibrations were observed in RA-FTIR spectra after metal deposition, but they did not provide an interpretation. Having addressed the reason for peak broadening, we now briefly discuss the effects of Cr or Ti. When a Cr or Ti adhesion layer is used before Au deposition, we observe a 60% or 70% decrease in peak intensity, indicating a loss of C–H bonds. This can be attributed to the highly reactive nature of Cr or Ti atoms that partially destroy the OTS film, in agreement with a previous study on Ti deposition on thiolate SAMs.<sup>11</sup> On the other hand, the presence of an adhesion layer seems to result in less broadening of the C–H stretch peaks. The fwhm of the  $\nu_a$  (CH<sub>2</sub>) peak is ~30–31 cm<sup>-1</sup> after metal deposition. The reaction of Cr or Ti with the OTS film in forming carbides likely introduces a diffusion barrier for metal penetration, resulting in less interaction of further deposited Au atoms with remaining fragments of alkyl groups.

The same approach can also be applied to metal–molecule–metal junctions. Here, we take advantage of the technique of surface-enhanced infrared absorption (SEIRA) spectroscopy.<sup>21</sup> We found that when a thin Au film of thickness <50 Å is deposited on H–Si(111), high-quality ATR-FTIR spectra can be obtained for thiol SAM films on the Au surface. This benefits from field enhancement on metal islands within the thin Au film. We choose MHA self-assembled multilayers<sup>17</sup> (see inset in Figure 3) to minimize the penetration of Au atoms from top contact deposition to reach the bottom Au surface. Figure 3 shows FTIR spectra of three-layer MHA on 30 Å Au/Si(111) before and after the deposition of the 800 Å thick top Au contact. Without the top contact, the spectrum is characterized by sharp  $\nu_a$  and  $\nu_s$  (CH<sub>2</sub>) peaks at 2916.0 and 2948.0 cm<sup>-1</sup>, indicating close-packed alkyl chains in all-trans configuration within the self-assembled multilayer. The peaks at 1711 and 1553 cm<sup>-1</sup> are C=O stretches in –COOH and –COO<sup>-</sup>, respectively.<sup>22</sup> After the deposition of 800 Å Au top contact, FTIR spectrum shows again broadening in  $\nu_a$  and  $\nu_s$  (CH<sub>2</sub>) peaks due to Au penetration. Even more significant broadening is seen in the C=O stretch region, suggesting strong interaction between Au atoms and carboxylic groups. There is also a loss of ~20% peak area in the C–H stretch region. Whether this results from conformation change or damage is not known at the present time.

The results presented above unambiguously establish the power and general applicability of ATR-FTIR in probing structure and conformation of molecules at buried interfaces in metal–molecule–semiconductor and metal–molecule–metal junctions. The extension of this methodology to functional junctions under bias is feasible and is clearly warranted. Of course, achieving this goal with reliability requires the verification of the quality of the metal contact layer, i.e., the absence of shorts due to extensive metal penetration into the film. In this regard, the recently developed method for metal deposition, nanotransfer printing,<sup>23</sup> is more attractive than thermal evaporation. This benign method for top metal contact formation can be coupled with multilayer film formation on metals or a number of chemical approaches for molecular functions on silicon to make the bias experiment feasible. One limitation is that the junctions shown here are of macroscopic size, while those in transport measurements are typically of microscopic dimension. Single-path surface FTIR in reflection or ATR geometry is well-known. Thus, it is possible to extend the approach to ~100 μm. This dimension is somewhat larger than those of typical molecular junctions, but the method should be of interest as a tool in mechanistic studies.

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**Supporting Information Available:** Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References

- Nitzan, A.; Ratner, M. A. *Science* **2003**, *300*, 1384–1389.
- Service, R. F. *Science* **2003**, *302*, 556–558.
- Chen, J.; Reed, M. A.; Rawlett, A. M.; Tour, J. M. *Science* **1999**, *286*, 1550–1552.
- Donhauser, Z. J.; Mantooh, B. A.; Kelly, K. F.; Bumm, L. A.; Monnell, J. D.; Stapleton, J. J.; Price, D. W., Jr.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **2001**, *292*, 2303–2307.
- Cui, X. D.; Primak, A.; Zarate, X.; Tomfohr, J.; Sankey, O. F.; Moore, A. L.; Moore, T. A.; Gust, D.; Harris, G.; Lindsay, S. M. *Science* **2001**, *294*, 571–574.
- Fan, F. R. F.; Lai, R. Y.; Cornil, J.; Karzazi, Y.; Brédas, J.-L.; Cai, L.; Cheng, L.; Yao, Y.; Price, D. W., Jr.; Dirk, S. M.; Tour, J. M.; Bard, A. J. *J. Am. Chem. Soc.* **2004**, *126*, 2568–2573.
- Collier, C. P.; Wong, E. W.; Belohradsky, M.; Raymo, F. M.; Stoddart, J. F.; Kuekes, P. J.; Williams, R. S.; Heath, J. R. *Science* **1999**, *285*, 391–394.
- Collier, C. P.; Matternsteig, G.; Wong, E. W.; Luo, Y.; Beverly, K.; Sampaio, J.; Raymo, F. M.; Stoddart, J. F.; Heath, J. R. *Science* **2000**, *289*, 1172–1175.
- Stewart, D. R.; Ohlberg, D. A. A.; Beck, P. A.; Chen, Y.; Williams, R. S.; Jeppesen, J. O.; Nielsen, K. A.; Stoddart, J. F. *Nano Lett.* **2004**, *4*, 133–136.
- Lau, C. N.; Stewart, D. R.; Williams, R. S.; Bockrath, M. *Nano Lett.* **2004**, *4*, 569–572.
- De Boer, B.; Frank, M. M.; Chabal, Y. J.; Jiang, W.; Garfunkel, E.; Bao, Z. *Langmuir* **2004**, *20*, 1539–1542.
- Walker, A. V.; Tighe, T. M.; Cabarcos, O. M.; Reinard, M. D.; Haynie, B. C.; Uppili, S.; Winograd, N.; Allara, D. L. *J. Am. Chem. Soc.* **2004**, *126*, 3954–3963.
- Wang, W.; Lee, T.; Kretzschmar, I.; Reed, M. A. *Nano Lett.* **2004**, *4*, 643–646.
- Kushmerick, J. G.; Lazorcik, J.; Patterson, C. H.; Shashidhar, R.; Seferos, D. S.; Bazan, G. C. *Nano Lett.* **2004**, *4*, 639–642.
- Sagiv, J. *J. Am. Chem. Soc.* **1980**, *102*, 92–98.
- Parikh, A. N.; Allara, D. L.; Azouz, I. B.; Rondelez, F. *J. Phys. Chem.* **1994**, *98*, 7577–7590.
- (a) Evans, S. D.; Ulman, A.; Goppert-Berarducci, K. E.; Gerenser, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 5866–5868. (b) Freeman, T. L.; Ulman, A. *Langmuir* **1995**, *11*, 4411–4417.
- Maoz, R.; Sagiv, J.; Degenhardt, D.; Mohwald, H.; Quint, P. *Supramolecular Science* **1995**, *2*, 9–24.
- Weaver, J. F.; Carlsson, A. F.; Madix, R. J. *Surf. Sci. Rep.* **2003**, *50*, 107–199.
- Fisher, G. L.; Walker, A. V.; Hooper, A. E.; Tighe, T. B.; Bahnck, K. B.; Skriba, H. T.; Reinard, M. D.; Haynie, B. C.; Opila, R. L.; Winograd, N.; Allara, D. L. *J. Am. Chem. Soc.* **2002**, *124*, 5528–5541.
- Goutev, N.; Futamata, M. *Appl. Spectrosc.* **2003**, *57*, 506–513 and references therein.
- Arnold, R.; Azzam, W.; Terfort, A.; Wöll, C. *Langmuir* **2002**, *18*, 3980–3992.
- Loo, Y. L.; Willett, R. L.; Baldwin, K. W.; Rogers, J. A. *J. Am. Chem. Soc.* **2002**, *124*, 7654–7655.

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