Interfacial Atomic Structure of a Self-Assembled Alkyl Thiol Monolayer/Au(111): A Sum-Frequency Generation Study

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Infrared-visible sum-frequency generation (SFG) is used to spectroscopically probe the interfacial structure of a self-assembled monolayer of alkyl thiol on a Au(111) surface. The SFG spectra of the CH_3 group measured as a function of azimuthal angle indicates that sulfur atoms cannot be situated at sites of a single type, e.g., hollow or bridge, but must be in a mixed arrangement. SFG is also used to study the reconstruction of the gold substrate by alkyl thiol.

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Nearly 10 years ago Nuzzo and Allara [1] discovered that when gold is immersed in a dilute organosulfur solution an organic monolayer is spontaneously chemisorbed on the surface of the gold, producing a self-assembled monolayer (SAM). Such coatings are potentially useful for corrosion inhibition, wear protection, and organic sensors. Perhaps the best characterized SAM system is $CH_3(CH_2)_{n-1}SH$ (C_n), adsorbed on a Au surface. The C_n/Au system, specifically its surface and chain orientation, has been widely studied. He [2] and x-ray [3] scattering studies have shown that the CH_3 outer surface has a rectangular unit cell which includes four tilted hydrocarbon chains. Infrared spectroscopy [4], in agreement with Raman scattering [5] and ellipsometry [6], as well as an earlier sum-frequency generation (SFG) study [7], suggests that the chains are densely packed and the number of the gauche defects is insignificant. Despite all the available experimental results, the location of sulfur chemisorption sites is known only by inference. The conventional belief has been that the S atoms reside at hollow sites of the gold substrate, generating a simple $(\sqrt{3} \times \sqrt{3})R30°$ structure. The location of these sites is essential for a detailed evaluation of Au-S, Au-Au, and S-S bonds at the interface. These in turn affect the monolayer orientation and stability.

Single frequency second-order nonlinear optical measurement has proven to be a unique technique for studying interface structural symmetry [8]. In this work infrared-visible SFG was used to probe the structural symmetry of the C_{18}/Au(111) interface. The present measurements in which the frequency dependence of the signal was used to differentiate the substrate and adlayer structures demonstrate the sensitivity of SFG *spectroscopy* to the structural symmetry of an interface. Our experiments reveal an unexpected threefold rotational symmetry at the sulfur adsorbate sites of the C_{18}/Au(111) system. This result precludes the sulfur atoms being located solely at single-type hollow sites of the gold substrate. Such a configuration would give rise to an isotropic SFG signal. Recently, we learned of an elegant x-ray experiment that independently produced results leading to the same conclusion [9]. The experimenters suggest a disulfide configuration with sulfur in the hollow and bridge sites. This arrangement would produce SFG results consistent with ours.

In addition to adsorbate site geometry, the effect of the thiol chemisorption on the surface stress of the gold substrate was also examined. Measured SFG rotational anisotropy of the gold substrate is consistent with $(\sqrt{3} \times 23)$ and (1×1) reconstruction patterns for air/Au(111) and C_{18}/Au(111). These measurements show that the surface lattice of clean Au(111) is stable in air and relaxes upon the chemisorption of S atoms.

Our samples consist of a monolayer of octadecanethiol (ODT) on a Au(111) single crystal. The gold substrate was cleaned in a UHV chamber and its surface contamination checked using XPS. The Au(111) substrate was then immersed into a 100 μM solution of ODT in ethanol for ~16 h. The SFG measurements were made in air with a visible laser beam at 532 nm and a tunable infrared beam, both beams incident at 60° in a counterpropagation geometry. In this arrangement, the resonant and nonresonant components of the nonlinear susceptibility are phase additive [10]. The infrared light was generated by stimulated Raman scattering of a doubled Nd:YAG pumped dye laser in a multipass H_2 cell [11]. A portion of the output of the doubled Nd:YAG laser was used as the visible light source. The incident light pulses had a duration of ~7 nsec and a fluence of ~ 15 mJ/cm^2 for both visible and IR beams. The intensity of the laser radiation was measured to be at least an order of magnitude below the sample damage threshold. Additionally, changes in the spectra of the system were not observed after a month of study with the same sample.

The frequency dependence of the ODT/Au(111) SFG signal is shown in Fig. 1. This spectrum was produced with p-polarized fundamental and SFG beams (*ppp* polarization) at $\phi = 37°$, where ϕ is the angle between a mirror plane of the Au(111)-(1×1) substrate and the plane of incidence. The SFG spectra exhibits a sharp feature at

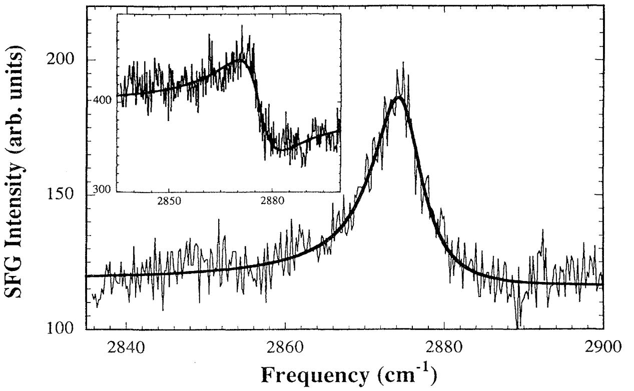

FIG. 1. SFG spectrum of ODT/Au(111) in *ppp* polarization at $\phi = 37°$. Inset: The same spectrum at $\phi = 7°$. The marked difference in the spectra results from the dependence of the relative phase between the nonresonant and resonance signals on the azimuthal angle ϕ.

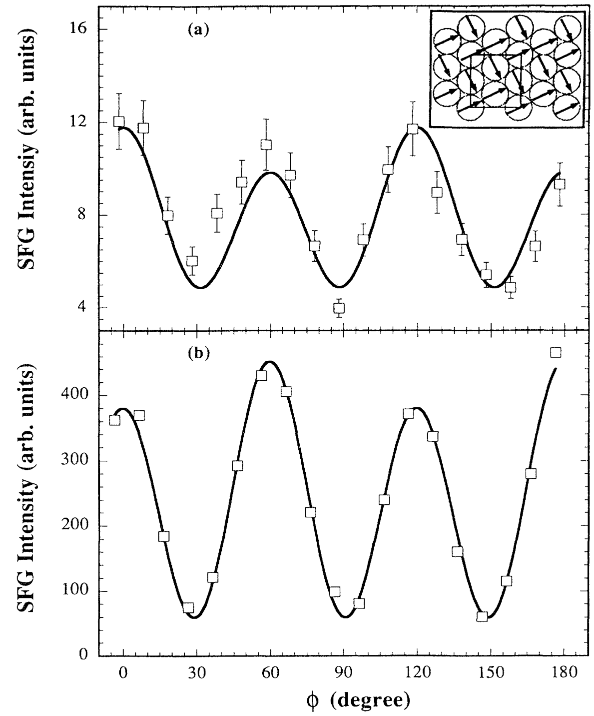

FIG. 2. (a) Resonant SFG intensity, $|A_R/\Gamma_R|^2$, and (b) nonresonant SFG intensity, $|A_{\rm NR}|^2$, of the ODT/Au(111) as a function of the rotation angle ϕ. These values are obtained by fitting the SFG spectra by Eq. (1) at various ϕ. Here ϕ is the angle between a mirror plane of the Au(111)-(1 × 1) and the plane of the incidence. The resonance SFG is generated solely by the CH_3 group at 2875 cm^{-1}, and the nonresonance SFG intensities represent signals at frequencies far from the resonance (i.e., $|\omega_R - \omega_{ir}|/\Gamma_R \geq 10$). The solid lines are the theoretical fit to the data. The error of $\sim 1\%$ is not shown in (b). Inset: Surface structure of C_{18}/Au(111). The rectangular unit cell contains four chains with two different chain configurations in each unit cell [2,3]. These hydrocarbon chains are related to one another by a rotation about the chain axis. The arrows indicate the direction of the C-C bonds at the methyl groups of the monolayer.

2875 cm^{-1} which was assigned to the symmetric stretch of the CH_3 group. The smooth solid line in Fig. 1 is the theoretical fitted to the experimental data using a standard model [12],

$$I^{\rm SFG} \propto \left| A_{\rm NR} + \frac{A_R e^{i\psi}}{\omega_R - \omega_{ir} + i\Gamma_R} \right|^2, \qquad (1)$$

where A_R, Γ_R, and ω_R are the strength, damping constant, and angular frequency of a single resonant vibration. $A_{\rm NR}$ and ψ are the nonresonant amplitude and the relative phase between the resonant and nonresonant signals, respectively. The SFG spectra of the ODT/Au(111) sample were measured at different azimuthal angles ϕ. Then each spectrum was fitted by Eq. (1). In this way, the angular dependence of the nonresonant, $|A_{\rm NR}|^2$, and resonant signals, $|A_R/\Gamma_R|^2$, was determined. Since the relative phase ψ varies as a function of ϕ, this procedure is essential for extracting the nonresonant and resonant contributions from the total measured intensity. The marked difference between the line shape of the SFG spectra taken at $\phi = 37°$ and $\phi = 7°$, shown in Fig. 1, clearly demonstrates the dependence of ψ on the azimuthal angle. As expected, the width of the resonance and its frequency were unchanged with respect to azimuthal rotation [13].

The resonant SFG signal is generated at the air/monolayer interface by CH_3 groups, and its dependence on the sample orientation is directly related to the position of the sulfur atoms at the Au interface. This results from the fact that the position of the S atoms, taken with a specific chain geometry, uniquely determines the position of the CH_3. A schematic of a surface unit cell of the system is shown in the inset of Fig. 2(a). The hydrocarbon chains are tilted approximately toward the next nearest neighbor (NNN) chain [3,4]. For a given chain, there are six NNN's which produce six different *tilt domains*. The tilt direction is the only difference between these domains. Since the topmost gold surface layer is hexagonally symmetric, a unit cell can also be oriented along different azimuthal directions to produce new *rotational domains*. These domains are related to each other by a rotation about the normal to the surface. For example, if all the sulfur atoms were located at single-type hollow sites of the gold surface, the rotated domains would be related to one another by a $n\pi/3$ rotation about the normal to the surface, where n is an integer.

Utilizing these relationships and the uniform distribution of all domains [14], we can calculate the total SFG polarization generated at the surface of the sample for a specific domain configuration. As shown in the inset of Fig. 2(a), the *surface* of each domain is C_1 symmetric. With both p-polarized infrared and visible beams the polarization of the SFG output, generated by the tilt domains, in the plane of incidence is

$$\sum_{\text{all tilt direction}} \mathbf{P} = \{ - E_{1z} E_{2z} \chi_{yzz} \sin(\phi) - E_{1x} E_{2x} [\chi_{xxy} \cos(\phi)^2 \sin(\phi) + \chi_{xyx} \cos(\phi)^2 \sin(\phi) + \chi_{yxx} \cos(\phi)^2 \sin(\phi) + \chi_{yyy} \sin(\phi)^3] + E_{1x} E_{2z} [\chi_{xxz} \cos(\phi)^2 + \chi_{yyz} \sin(\phi)^2] + E_{1z} E_{2x} [\chi_{xzx} \cos(\phi)^2 + \chi_{yzy} \sin(\phi)^2]\} \hat{\mathbf{x}} + \{E_{1z} E_{2z} \chi_{zzz} - E_{1x} E_{2z} \chi_{zyz} \sin(\phi) - E_{1z} E_{2x} \chi_{zzy} \sin(\phi) + E_{1x} E_{2x} [\chi_{zxx} \cos(\phi)^2 + \chi_{zyy} \sin(\phi)^2]\} \hat{\mathbf{z}} . \tag{2}$$

Here, χ_{ijk} is the second-order nonlinear susceptibility element and $\mathbf{P}$ is the SFG polarization vector in the plane of incidence produced by a single domain. The unit vector $\hat{\mathbf{x}}$ ($\hat{\mathbf{y}}$) is parallel to the short (long) side of the rectangular unit cell, and $\hat{\mathbf{z}}$ is normal to the surface; see the inset in Fig. 2(a). If all the S atoms were located at single-type hollow sites of the gold surface, the total resonant SFG intensity, I^{SFG}, would be

$$I^{\mathrm{SFG}} \propto \left| \sum_{n=0}^{n=5} \sum_{\text{all tilt directions}} \mathbf{P}(\phi + n\pi/3) \cdot \hat{\mathbf{e}}(sfg) \right|^2 = C_0 , \tag{3}$$

where $\hat{\mathbf{e}}(sfg)$ is the unit vector in the SFG polarization direction and C_0 is a constant, independent of ϕ, and hence the signal is isotropic. The same results are obtained if all the S atoms reside at bridge or top sites of the substrate.

The variation of the resonant SFG intensity as a function of the azimuthal angle is shown in Fig. 2(a). These signals are generated solely by the CH_3 group at 2875 cm^{-1}. Our data are not isotropic but exhibit a threefold symmetric pattern which shows that the S atoms cannot all be at the same sites of the Au(111) surface. To generate such threefold symmetry, the sulfur atoms must be located either at bridge and hollow sites, at two different bridge sites, or at two different hollow sites [15]. These new geometries only allow $2n\pi/3$ rotations of the unit cell. The resonant signal intensity, I^{SFG}, can be expressed as

$$I^{\mathrm{SFG}}(\phi) = \left| C_1 e^{i\psi} \sum_{n=0}^{n=2} \sin^3(\delta + \phi + 2n\pi/3) + C_2 \right|^2 . \tag{4}$$

Here C_1 and C_2 are constants which are related to the second-order susceptibilities, δ is an angular offset, and ψ is the relative phase. The solid line in Fig. 2(a) is our best fit of the resonant intensity by Eq. (4) and is in good agreement with our model.

The new geometry of the sulfur sites requires gauche conformations in the hydrocarbon chains to maintain the observed spacing of the CH_3 groups at the air/monolayer interface. Surface Raman scattering [5] indicates that the S-C bond is approximately parallel to the gold surface; and molecular dynamics simulation [16] shows that when the angle between the S-C bond and the surface normal is restricted to 100° the first dihedral angle is 99% gauche and the chain becomes L shaped. This chain geometry which was observed in the *B* form of stearic acid [17] could explain the missing vibrational resonant signal of the CH_2 symmetric stretch in the C_{18}/Au(111) spectrum at 2853 cm^{-1} (see Fig. 1). We know that an all *trans* chain with an even number of CH_2 moieties is centrosymmetric and does not produce an SFG signal [18]. The hydrocarbon chains in ODT/Au(111) contain an odd number of methylene groups. If the chains were all *trans,* we would expect to observe the vibrational resonant signals of CH_2 at 2853 cm^{-1}. However, in the L shaped model the CH_2 moiety at the "kink" in the "L" is extremely close to the Au surface, and its stretch is nearly parallel to it, producing a broadened and highly diminished SFG response. The remaining even number of CH_2 moieties are in an all *trans* conformation and do not contribute to the SFG signal.

We turn our attention next to the atomic structure of the gold substrate at the interface of the ODT/Au(111) system. In Fig. 2(b) we plot the nonresonant SFG intensity deduced from our fit, $|A_{\mathrm{NR}}|^2$, as a function of ϕ in *ppp* polarization. Although the nonresonant intensity, which is the principle signature of the Au substrate, does not contain measurable contributions from vibrational resonances, it can contain contributions from higher-order bulk nonlinearities and from the Au-S bonds. The higher-order bulk nonlinearities are small and can be ignored [19]. The Au-S bond density is substantially smaller than the density of the Au atoms at the surface of the gold. In addition, the photon energy of the visible beam is far from the electronic transition of the Au-S bond [20] but is close to the optical interband edge in the Au substrate at 2.35 eV [21]. Experimentally, this was checked by measuring the intensity of SFG signals from the bare Au surface. The intensity is approximately the same as the nonresonant intensity found with the ODT/Au(111) system. Based on these facts, we assigned the nonresonant SFG signal to the Au surface. As shown in Fig. 2(b), the variation of the nonresonant signal with ϕ in *ppp* polarization is threefold symmetric and is in good agreement with the theoretical fit, depicted by the solid line, based on C_{3v} surface symmetry.

To study the effect of thiol adsorption on the gold surface structure, the SFG intensity at 2800 cm^{-1} was measured in *sss* polarization as a function of ϕ for both air/Au(111) and ODT/Au(111) systems. The results, shown in Fig. 3, show a marked difference between the gold surface structure before and after the thiol adsorption. This difference is understood in the following context: A clean surface of gold (111) has three rotational domains generated by a rectangular ($\sqrt{3} \times 23$) unit cell at room temperature. This reconstruction was observed

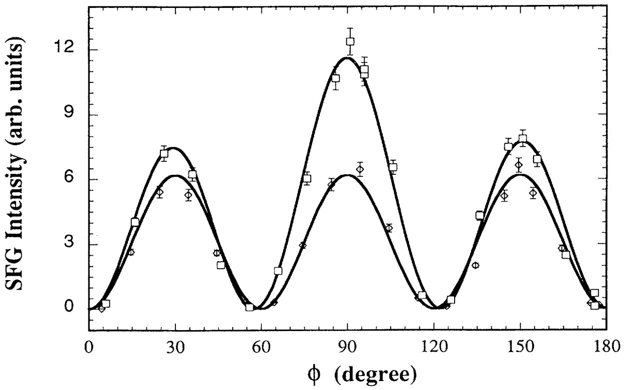

FIG. 3. Variation of SFG intensity with azimuthal angle ϕ at 2800 cm^{-1} in *sss* polarization for ODT/Au(111) (◇) and air/Au(111) (□). The solid lines are the theoretical fit based on $(1 \times 1)C_{3v}$ structure for ODT/Au(111) and $(\sqrt{3} \times 23)$ structure for air/Au(111).

by electron, He, and x-ray scattering, as well as by scanning tunneling microscopy under UHV conditions [22–25]. The reconstruction is caused by a stressed top surface layer. The surface layer relaxes upon the adsorption of thiol and produces a C_{3v} symmetric (1×1) structure. The solid lines in Fig. 3 are the theoretical fit using threefold (1×1) and onefold $(\sqrt{3} \times 23)$ symmetric unit cells for ODT/Au(111) and air/Au(111) systems, respectively. Agreement between the experimental results and the model is excellent and illustrates that the $(\sqrt{3} \times 23)$ structure of a clean gold surface is stable in air, for at least the three hours of the measurement time.

In summary, SFG spectroscopy has been used to study the interfacial structure of an ODT/Au(111) system. The substrate and adsorbate structures were differentiated by utilizing the frequency dependence of the technique. Our results corroborate a new model for the sulfur sites at the interface and show that the sulfur atoms are not all located at the hollow sites of the Au(111) substrate. A distinctive structure for a clean Au(111) surface in air and the gold substrate surface at the ODT/Au(111) interface was found. Our measurements show that the $(\sqrt{3} \times 23)$ structure of the Au(111) surface is stable in air. This structure changes to (1×1) after chemisorption of alkyl thiol on the surface.

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[13] As an additional test of the single resonance model, the variation of SFG intensity at three frequencies far from resonance, 2800, 2750, and 3000 cm^{-1}, was also measured as a function of ϕ and found to have the same dependence as $|A_{\mathrm{NR}}|^2$.

[14] The domain size is ~100 Å [3] and our laser spot size of ~2 mm contained ~10^{10} domains.

[15] There are two different hollow sites on a (111) fcc surface. The difference between these sites is the presence or absence of a second layer atom directly below the sites.

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