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Direct observation of sulfur dimers in alkanethiol self-assembled monolayers on Au(111)

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High-resolution electron-energy-loss spectra of octadecanethiol self-assembled monolayers (SAM's) on Au thin films have been obtained after annealing the sample to various temperatures. Annealing to 375 K results in the appearance of the S-S stretch at 530 cm^{-1}, a direct observation of sulfur dimers for alkanethiol SAM's adsorbed on Au. The appearance of dimers following annealing is explained by the presence of an activation barrier to the formation of gauche defects at the S-C bond. [S0163-1829(99)51016-3]

Self-assembled monolayers are thin organic films that form spontaneously on solid surfaces. They are widely studied because of their importance in wetting phenomena, tribology, chemical sensing, and nanotechnology.[1–4] Much debate still surrounds the formation and structure of what is probably the most widely studied self-assembled monolayer (SAM) system of all, that of alkanethiols $[\mathrm{CH_3(CH_2)}_{n-1}\mathrm{SH}]$ on Au(111). It is known that the S-H bond cleaves and the molecule chemisorbs to the surface through a covalent Au-S bond while the hydrocarbon chains interact laterally through van der Waals attraction.[5] A key issue that remains unresolved concerns the existence of disulfide bonds between adjacent head groups. The sulfur atoms were originally though to occupy the threefold hollow site on the Au(111) surface [see Fig. 1(a)]. A disulfide bond is incompatible with this configuration. Subsequent grazing incidence x-ray diffraction (XRD) studies[6] have reported that molecules occupy two different sites, as shown in Fig. 1(b).[7] Since the sulfur atoms in these sites are spaced 2.2 Å apart, the existence of a S-S bond between adjacent head groups has been proposed.[6] The disulfide bond, however, has not been observed on the surface directly. Temperature programmed desorption (TPD) studies[8,9] have observed desorption of dialkyl disulfide species, but whether these species existed on the surface or were formed during the desorption process could not be established. Adding to the debate are recent reports that the monolayers are damaged by exposure to x rays,[10] including changes in the sulfur head group bonding that result in the formation of disulfides.[11]

Vibrational spectroscopies are well suited for the detection of chemical bonds. Among these spectroscopies, high-resolution electron-energy-loss spectroscopy (HREELS) is especially versatile since it can excite and detect both infrared- and Raman-active vibrational modes.[12] In this Rapid Communication, we report the direct observation of S-S dimers for the system of alkanethiols adsorbed on Au. The presence of the dimers is indicated by the S-S stretch in the electron-energy-loss spectrum of the monolayer. The S-S stretch is observed *only* after the sample has been annealed to 375 K, suggesting that there is an activation barrier to the formation of the sulfur dimer. The presence of this barrier can be explained by the energetic cost of forming gauche defects at the S-C bond as required by the dimer model [Fig. 1(b)].

Samples were prepared from Au thin films (approximately 1.5-μm thick) deposited on GaAs. A sacrificial silicon oxide layer protected the surface against contamination until the time of use. The oxide layer was removed by etching in concentrated hydrofluoric acid for 5 min. Atomic force microscopy following the HF etch showed that the Au films consisted of large (approximately 1000 Å) crystalline grains terminated with the (111) face. Immediately after removal of the sacrificial oxide layer, the samples were placed in a 1-mmol solution of octadecanethiol ($n=18$) (Aldrich, 98%) in ethanol for 24 h. Upon removal from solution the samples were rinsed in ethanol and dried with nitrogen. Octadecanethiol monolayers had a water contact angle of 110°.

Samples were introduced into ultrahigh vacuum by means of a load lock system. Both the UHV chamber and the load lock have been described in detail previously.[13] HREEL spectra were obtained using the LK3000 spectrometer in specular mode at an incident energy of 6 eV. Spectral resolution was on the order of 40 cm^{-1} (full width at half maximum of the elastic peak) at a count rate on the order of 10^5 cps. Spectra were recorded with the sample at approximately 120 K. For annealing experiments, the sample was held at a given temperature for 5 min, then cooled to 120 K to obtain the spectrum.

Figure 2 shows the HREEL spectrum for an octadecanethiol monolayer on Au. Peak assignments are listed in

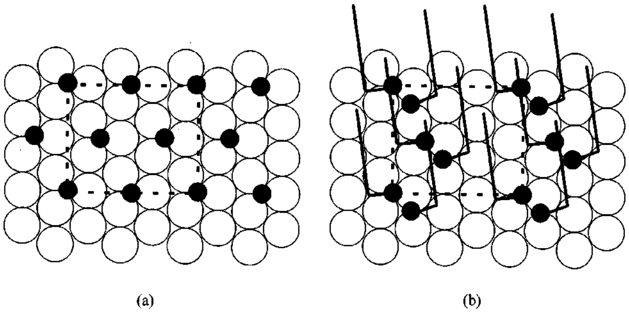

FIG. 1. Schematic of adsorption sites for alkanethiols on Au(111). In (a) the sulfur atoms adsorb at the threefold hollow sites and dimers are not formed. The chains are straight (at low temperature), and are not shown for clarity. In the proposed dimer arrangement (b), one sulfur atom sits in the threshold hollow site, and the other sits near the bridge site (Ref. 6). A gauche defect exists at the S-C bond. The dashed rectangle represents the unit cell of the dimerized structure.

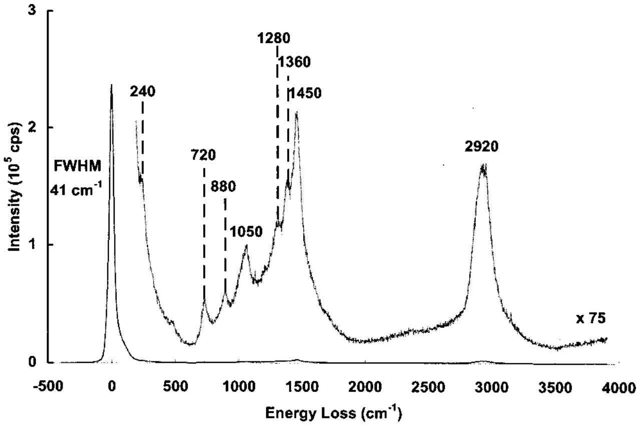

FIG. 2. HREEL spectrum of octadecanethiol self-assembled monolayer adsorbed on a thin film of Au.

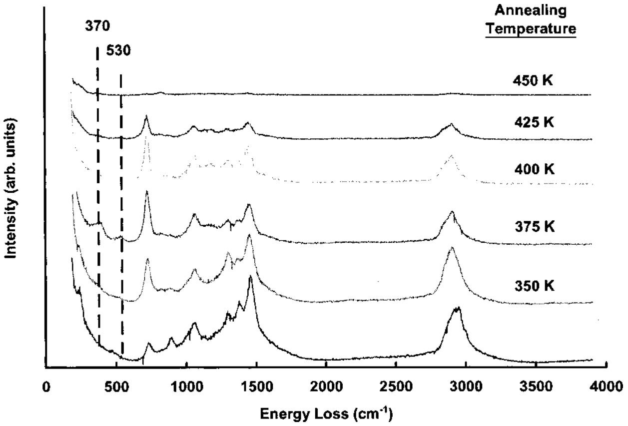

FIG. 3. HREEL spectra of an octadecanethiol self-assembled monolayer as a function of annealing temperature.

Table I. The spectrum is dominated by the C-H stretch at 2920 cm^{-1} and CH bending modes. The positions of these peaks are in agreement with those previously observed for straight chain alkanes[14,15] and alkanethiol self-assembled monolayers on Au.[16] Also present is the C-C stretch at 1050 cm^{-1}.[15] The peak at 240 cm^{-1} is assigned to the Au-S stretch.[5] The small peak at about 480 cm^{-1} is attributed to a double loss of the Au-S stretch.

Figure 3 shows HREEL spectra of octadecanethiol monolayers as a function of annealing temperature. The monolayers have completely desorbed upon annealing to 450 K, shown by the disappearance of the C-H modes. Prior to monolayer desorption, several important features are observed in the HREEL spectra. Upon annealing to 350 K three changes occur. The peaks at 880 and 1360 cm^{-1}, which are both CH_3 bending modes,[14–16] decrease in intensity. At the same time, the C-H stretch shifts from about 2920 to 2880 cm^{-1}, indicating that there is less contribution from the CH_3 stretching modes relative to the CH_2 stretching modes. Last, the intensity of the peak at 720 cm^{-1} increases dramatically. This peak is a CH_2 bend that arises for chains of methylene groups greater than four carbon atoms long.[14] The changes in the spectra indicate that the underlying parts of the chains are now more accessible to the incident electron beam. These changes are attributed to a change in the structure of the film, which is tightly packed at room temperature, but considerably more open at 350 K due to partial desorption of the monolayer. This partial desorption results in the appearance of striped phases, characteristic of low coverage structures, observed in several scanning tunneling microscopy (STM) studies.[8,17,18]

TABLE I. Peak assignments for aklanethiol monolayers on Au.

Peak position (cm^{-1})	Assignment	References
2920	C-H stretch	14,16
1450	CH_2 scissor	14–16
1360	CH_3 symmetric bend	14–16
1280	CH_2 twist-rock	14,15
1050	C-C stretch	15
880	CH_3 rock	14,15
720	CH_2 rock-twist	14,15
580	SO_2 scissor	21
540	S-S stretch	5,14
370	S-S-C bend	22
240	Au-S stretch	5

Although according to STM observations the film structure does not change qualitatively upon annealing to 375 K,[17] the HREEL spectrum does: a peak appears at 530 cm^{-1} which we assign to the S-S stretch. This mode is typically observed in the range from 500 to 540 cm^{-1}.[14] For example, for liquid diallyl disulfide[19] and liquid dimethyl disulfide,[20] the S-S stretch appears at about 510 cm^{-1}. This mode has also been reported at about 500 cm^{-1} in HREEL spectra of dimethyl disulfide multilayers on Au.[5]

We have considered alternative assignments for this peak, but have concluded that none is viable. The most likely candidates are those arising from hydrocarbons or a combination of sulfur, carbon, and gold atoms. The peak is not likely to be due to straight chain hydrocarbon species, since these molecules (octadecane, for example) do not have any modes between 400 and 600 cm^{-1} in either Raman or infrared spectra.[21] Alkenes have vibrational modes in this region, but the absence of the sp^2 C-H stretch at 3050 cm^{-1} and the C$=$C stretch at 1700 cm^{-1} in the spectra following annealing to 375 K rules out the presence of alkenes. Some branched hydrocarbons also have vibrational modes in the 400–600 cm^{-1} region, but it is highly unlikely that branched chains would result from low-temperature annealing of the monolayer. Thus, the possibility that the peak at 530 cm^{-1} is due to a hydrocarbon mode is ruled out. Furthermore, the C-S stretch appears in the region between 680 and 720 cm^{-1},[5,14] and the Au-S bond is observed at 240 cm^{-1}.[5] One possibility is oxidation of the sulfur head group, resulting in sulfur-oxygen bonds at the surface.[22] Such a species would be expected to result in peaks at about 1130 and 1300 cm^{-1} due to the S$=$O stretch, at 610 to 545 cm^{-1} due to the SO_2 scissor mode, and 525 to 495 cm^{-1} due to the SO_2 wagging mode.[14] While the presence of the S$=$O stretching modes at 1130 and 1300 cm^{-1} would be masked by the intense C-H and C-C modes, it is important to determine that the peak at 530 cm^{-1} is not due to the scissor or wagging modes (even though there is poor agreement with the expected positions of these peaks). To this end we have examined decanethiol ($n=10$) monolayers following exposure to air for a few days. The HREEL spectrum [Fig. 4(a)] shows a peak at 580

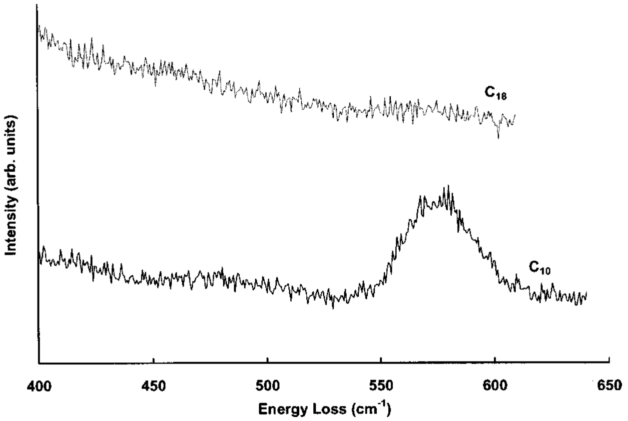

FIG. 4. HREEL spectra for alkanethiol self-assembled monolayers exposed to air for a few days. In the spectrum of decanethiol (a) a peak is present a 580 cm^{-1} that is attributed to a sulfur-oxygen mode. This mode is absent in the spectrum for octadecanethiol.

cm^{-1}, consistent with the SO_2 scissor mode of oxidized sulfur. The same peak was *not* present for an octadecanethiol sample exposed to air for the same length of time [Fig. 4(b)], indicating that the longer chains more effectively protected the sulfur head groups from oxidation. These experiments demonstrate that the peak observed at 530 cm^{-1} is not due to oxidation of the sulfur head group. Thus, the S-S stretch is the only logical assignment for this peak.

Also upon annealing to 375 K, an additional peak appears at 370 cm^{-1}.[23] This peak is present at the same annealing temperatures as the S-S stretch, suggesting that it is related to the S-S bond. Molecules such as dimethyl disulfide in the liquid phase exhibit peaks at 240 and 270 cm^{-1} which are attributed to S-S-C bending modes.[24] At first glance, then, it would appear that the peak at 370 cm^{-1} is too high in energy to be assigned to the S-S-C bend. Skeletal modes, however, show a wide variation in position depending on conformation. For example, the position of the C-C-C bend in the gauche conformation of allyl halides varies 40 to 170 cm^{-1} from the cis conformation.[19] In addition, even after S-S bond formation, one may expect a significant interaction between the sulfur head group and the metallic substrate that could blueshift in the S-S-C bending frequency. Such a shift is observed for dimethyl disulfide adsorbed on Cu(100) for which the S-S-C bend is observed at 300 cm^{-1};[25] thus a significant shift in the S-S-C bend for disulfide on Au is quite reasonable. Combined with the fact that the behavior of this peak follows that of the S-S stretch, the peak at 370 cm^{-1} is assigned to the S-S-C bending mode.[26]

The observation of the S-S stretch after low-temperature annealing of the monolayer has significant implications for the formation mechanism of alkanethiol SAM's. In the proposed model for sulfur dimers, a gauche defect exists at the S-C bond.[6] For *n*-alkanes in the liquid state, the activation barrier for transition from trans to gauche conformations is on the order of 3 kcal/mol. This value is low enough that the gauche fraction of polyethylene at 298 K is estimated to be 0.38.[27] For densely packed films, however, a larger barrier exists because neighboring chains must also be displaced. This barrier was estimated by molecular dynamics simulations to be 11 kcal/mol in a densely packed hydrocarbon film.[28] Especially relevant to the interpretation of the present experiments is the molecular dynamics (MD) work of Mar and Klein.[29] They simulated a system of pentadecanethiol chains, while constraining the S atoms to sit on the threefold hollow sites of the Au(111) surface (hence, disulfide bonds were not allowed to form). These authors estimated the density of gauche defects at room temperature to be about 4%; furthermore, these defects are concentrated at the vacuum-monolayer interface.[29] While at room temperature there are no defects at the first C-C bond (the one closest to the Au interface), and at 370 K the density of defects at those bonds is still less than 3%, at 391 K the density reaches almost 9%, signaling that these defects can penetrate into the film with ease at this temperature. Relieving the constraint on the S atoms could arguably result in a much larger concentration of defects at the S-C bond.

Based on XRD studies, it has been proposed that the self-assembly process is kinetically limited, such that immediately following monolayer formation, a nonequilibrium structure exists that contains many domain walls and is disordered.[30] In the subsequent XRD study that proposed the presence of the sulfur dimers,[6] the monolayers were annealed before being examined in order to remove disorder from the self-assembly process. In the present study, HREEL spectra show the presence of the S-S stretch after annealing to 375 K. These observations, combined with the information concerning the formation of gauche defects, suggest the following picture for adsorption of alkenethiols on Au(111).

At room temperature the chains adsorb in a nonequilibrium configuration. This configuration presumably consists of thiolate species chemisorbed in the threefold hollow sites of the Au surface, as originally proposed, and of some weakly bound (physisorbed) interstitial chains, as evidenced by TPD.[9] The resulting monolayer is well packed but is characterized by relatively small domain sizes. At this point the formation of a gauche defect at the S-C bond is energetically unfavorable. Annealing to relatively low temperatures (350 K) results in an increase in domain size as disorder from the self-assembly process is removed, along with partial desorption of the more weakly bound chains. Thus, steric restraints to gauche defect formation are reduced.[31] Our data show that for octadecanethiols self-assembled on Au(111) further annealing to about 375 K is needed for the chains to overcome the activation barrier to formation of gauche defects at the S-C bond and form S-S dimers at the Au surface.

In conclusion, the thermal behavior of alkanethiol SAM's on Au has been examined using HREELS. The appearance of the dimers following annealing to 375 K is consistent with initial adsorption of the alkanethiols in a nonequilibrium configuration in which the chains are unable to overcome the activation barrier for the formation of the gauche defect at the S-C bond.

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