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Letters

Thermal Healing of Self-Assembled Organic Monolayers: Hexane- and Octadecanethiol on Au(111) and Ag(111)

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The morphology of self-assembled hexane- and octadecanethiol monolayers on Au(111) and Ag(111) has been studied by variable temperature scanning tunneling microscopy. The depressions observed in the STM topographs of the films have been identified as substrate vacancy islands generated by chemical erosion during the self-assembly process. The defects can be healed out by thermal annealing at 350 K.

In self-assembled monolayers (SAMs), one exploits the fact that constituent molecules possess the unique ability to attach to solid surfaces by their head group, leaving their molecular tail free for functionalization purposes. Therefore, SAMs with a properly chosen functional group are essential ingredients to perform controlled modifications of surface properties like wettability, adhesion, lubrication, and corrosion.[1] Many interesting and detailed scanning probe studies of the alkanethiol/Au(111) systems have been undertaken recently. The relative ease of the synthesis of high-quality alkanethiol assemblies on Au(111) has largely contributed to the popularity of this rewarding model system.[2] Besides conventional STM experiments,[3–5] some more sophisticated scanning probe experiments have been done, including simultaneous force gradient and topographic measurements,[6] third harmonic generation,[7] and topographic deconvolution.[8] On the other hand, the study of the collective properties and mass transport in these systems seems to have attracted less attention and their understanding calls for further investigations. Self-assembly relies on a subtile balance between inplane and interfacial interactions. In particular, the occurrence of crystalline imperfections and domain walls within the monolayer as well as adsorbate induced defects in the substrate determine to a large extent the kinetics and thermodynamics of these layers. While temperature has been emphasized to play a leading role in further rearrangement of as deposited monolayers (chemisorbed layers),[2,9] the mechanisms by which these rearrangements take place have not been fully distangled yet. In the present letter we report on in situ STM studies of the thermal healing of self-assembled monolayers of alkanethiols on Au(111) and Ag(111). We show how this technique can be used to improve the quality of the layers. We also present unambiguous evidence that the depressions observed by STM in thiol-covered gold surfaces have

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their origin in the chemical erosion of gold atoms in the topmost gold layer.

The STM experiments have been done with a home-built "beetle-type" microscope. This stand-alone STM configuration is particularly versatile and permits an easy thermal coupling of the sample holder to a Peltier element for in situ variable temperature experiments (250–400 K).[10] As substrates we used gold (silver) films epitaxially grown on mica in vacuum. Before the self-assembly the samples have first been submitted to a flame annealing procedure. The gold (silver) layers were annealed in a butane–oxygen flame (hydrogen–oxygen in the case of silver) and quenched in ethanol. The effectiveness of this process was verified subsequently by STM examination revealing the presence of large 100 to 200 nm wide, defect-free terraces. The surfaces were of the (111) type as could be inferred from atomic resolution topographic images. After a second flame annealing, self-assembled monolayers of thiols (either hexane- or octadecanethiols) were prepared by immersing the substrates in a 1 mM solution of thiols in ethanol for times varying between minutes and several hours (up to 50 h) and final rinsing in ethanol. Only highest quality products from Aldrich and high-purity, low water content ethanol were used. In order to check the specificity of our preparation, selected samples were dried and transferred to an ultrahigh vacuum (UHV) surface analysis chamber where their surface composition was checked by Auger electron spectroscopy (AES) both after the flame annealing and after thiol self-assembly. We found that the flame-annealed epitaxial gold layers were of high purity (only containing trace amounts of carbon similar to what was detected on a heat-treated and sputtered monocrystal of gold). On the other hand, clear carbon and sulfur Auger peaks are detected after the self-assembly indicating the presence of adsorbed thiol molecules. The STM images shown in Figures 1 and 3 were recorded in the differential mode, which means that the derivative of the lines of constant tunnel current is recorded, whereas Figure 2 shows STM images with the gray scale representing the absolute tip height. The STM images 1 and 3 thus present the surface morphology as it appears when illuminated from the left-hand side. All images are raw experimental data without any image processing.

Thiol passivated gold substrates are known to be very stable against contaminants and could therefore be imaged in air. Alkanethiol monolayers on silver, on the other hand, are more subject to oxidation and have therefore been imaged in situ (in the hexanethiol solution). The thiol molecules are readily found to adopt on Au(111) the characteristic brushlike arrangement of the alkyl chains,[2,3] with the sulfur head groups ordering into a $(\sqrt{3}\times\sqrt{3})$-$R30°$ structure as demonstrated in the inset of Figure 2a revealing this ordering. The $\sqrt{3}$ ordering has been found to be perfect, however, only on a rather local scale of a few tens of an angstrom disturbed by irregular networks of antiphase domain boundaries.[9,10] On a larger scale, in addition depressions 1 to 3 nm in diameter are observed by STM. We have prepared monolayers of short (hexanethiol) and longer (octadecanethiol) molecules on Au(111) for various residence times of the samples in solution. As shown in Figure 1 the size and surface density of holes do not seem to depend on the length of the molecules used in the self-assembling process. Furthermore, no difference could be detected between layers that have been formed after a few minutes and several hours (up to 59 h), whether in the hole formation or in their healing dynamics. These results are in good agreement with a recent second harmonic generation study of the adsorption dynamics[11] that showed that for much lower concentrations of $45\,\mu$M a full monolayer is already formed in less than 10 s. Of course, further rearrangement is needed but is achieved reasonably after a few minutes to an hour. No holes could be seen by STM in a blank reference experiment in which a gold sample was dipped in pure ethanol for various amounts of time.

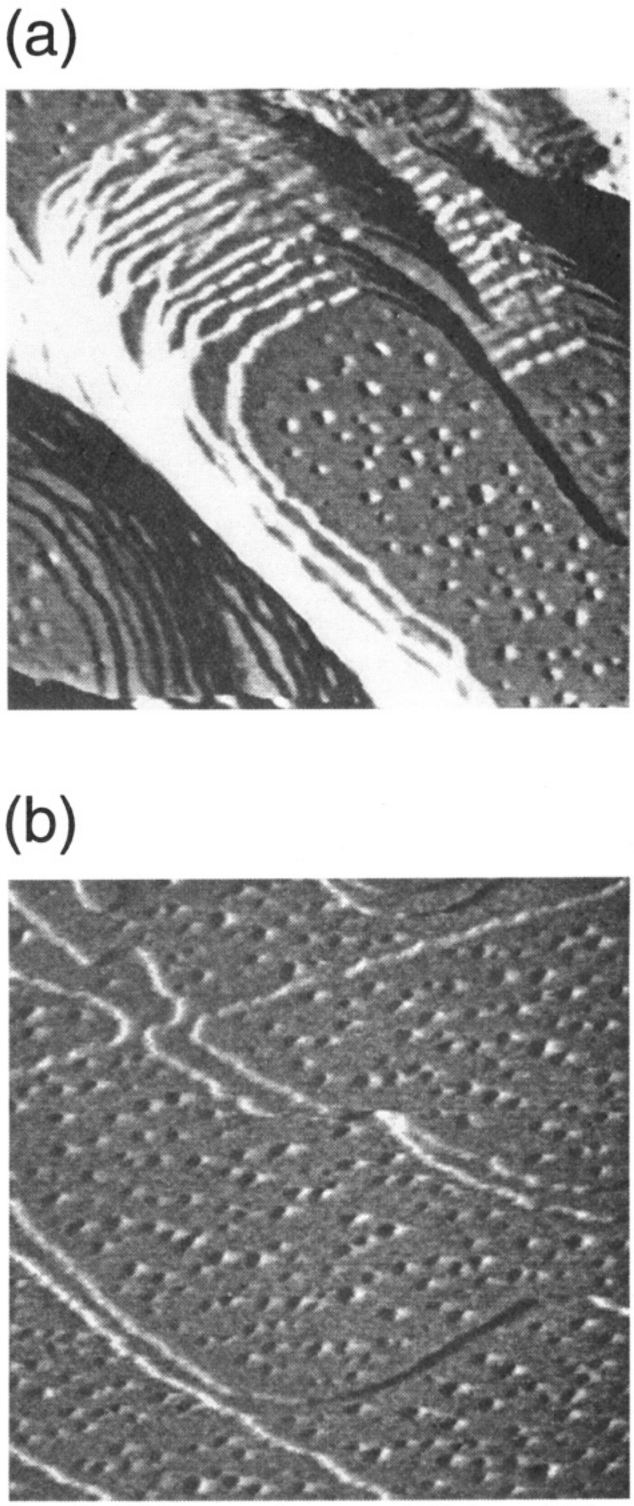

Figure 1. STM images of as-prepared (a) hexanethiol on Au(111), u = 0.57 V, i = 0.7 nA, and (b) octadecanethiol on Au(111). Images are 180 nm × 180 nm. Samples have been immersed for (a) 59 h and (b) 1 h. T = 300 K.

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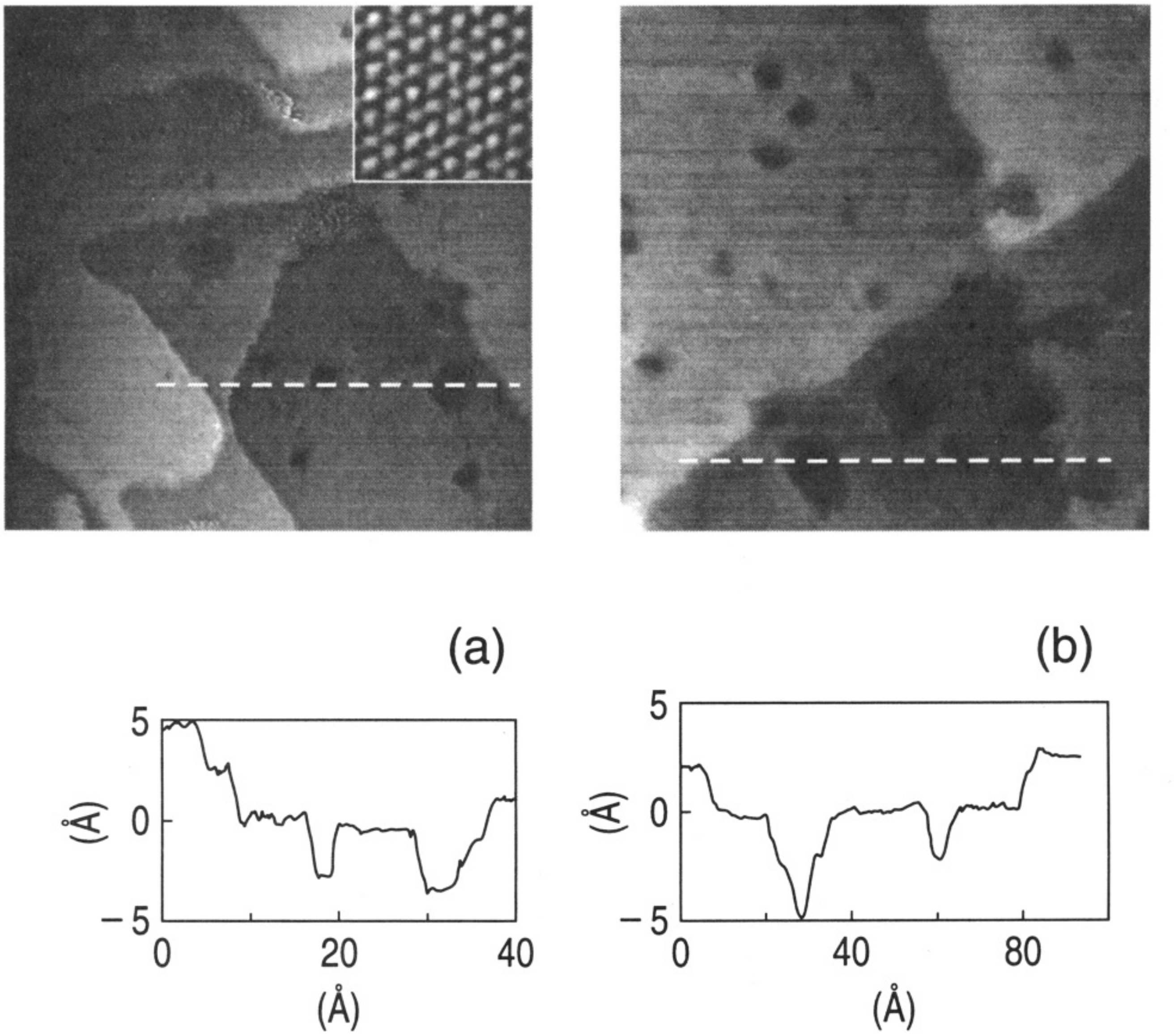

Figure 2. STM topographic images and cross sections of holes formed during hexanethiol self-assembly on (a) Au(111), image 60 nm × 60 nm, $u = 1.1$ V, $i = 1.1$ nA, and (b) Ag(111), image 120 nm × 120 nm, $u = 50$ mV, $i = 1.6$ nA. Samples have been immersed for (a) 1 min and (b) 5 min in the 1 mM hexanethiol/ethanol solution. $T = 300$ K. The inset in part a shows a high resolution image with the characteristic $(\sqrt{3}\times\sqrt{3})R30°$ structure adopted by the sulfur head groups.

The nature of the holes is a matter of controversial discussion.[4–8] The suggested explanations include the accumulation of "gauche" defects within the thiol layer,[4,6] defects in the topmost substrate layer[5,6] caused by erosion of gold atoms, and electronic effects.[8] Our high resolution images of thiols/Au(111) reveal the same $(\sqrt{3}\times\sqrt{3})R30°$ sulfur head-group structure at the bottom of the depressions as on the terraces (STM images are similar to those shown in the inset of Figure 2a); therefore we can eliminate straight away the idea that holes would simply be due to an absence of molecules. In order to gain additional insight into the nature of these depressions, we decided to study their topography. Figure 2 shows topographic images, not corrected for elastic deformations,[8] of hexanethiol on Au(111) and Ag(111), respectively. The lower part of Figure 2a shows topographic profiles accross a hexanethiol-coated gold surface. A quantitative analysis of the line-scan reveals that the depth of the depressions is equivalent to the height of a Au-substrate step ($h = 2.35$ Å) present on the left side of Figure 2a. This observation together with the fact that the bottom of the holes are decorated too with thiol molecules (as indicated by the observation of the $\sqrt{3}$ sulfur head group structure) strongly supports a "substrate" origin of the observed pitting. Our observation that octadecanethiols form similar depressions that are again identical in depth with the thickness of a Au(111) layer definitely rule out the idea that molecular defects could be the origin of the depression. The "substrate" nature of the holes is even more obvious in the case of hexanethiols on Ag(111). While holes induced by thiols on Au(111) are exclusively confined to the outermost gold substrate layer, those induced on Ag(111) extend to subsurface layers. In the topographic image and in the line scan of Figure 2b, steps of the silver substrate are clearly visible inside the hole. The substrate vacancy islands are likely to be formed by chemical erosion during the self-assembly process. Thiols are well-known to form mercaptide complexes with the noble metals,[12] which are highly soluble in organic solvants. A chemical analysis of the thiol/ethanol solution during the self-assembly process has indeed shown a continuously increasing gold content with assembling time.[5] The chemical attack of the second substrate layer in the case of Ag(111) is in agreement with

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(12) Holleman-Wiberg *Lehrbuch der Anorganischen Chemie*; Walter de Gruyter: Berlin, 1976; p 810.

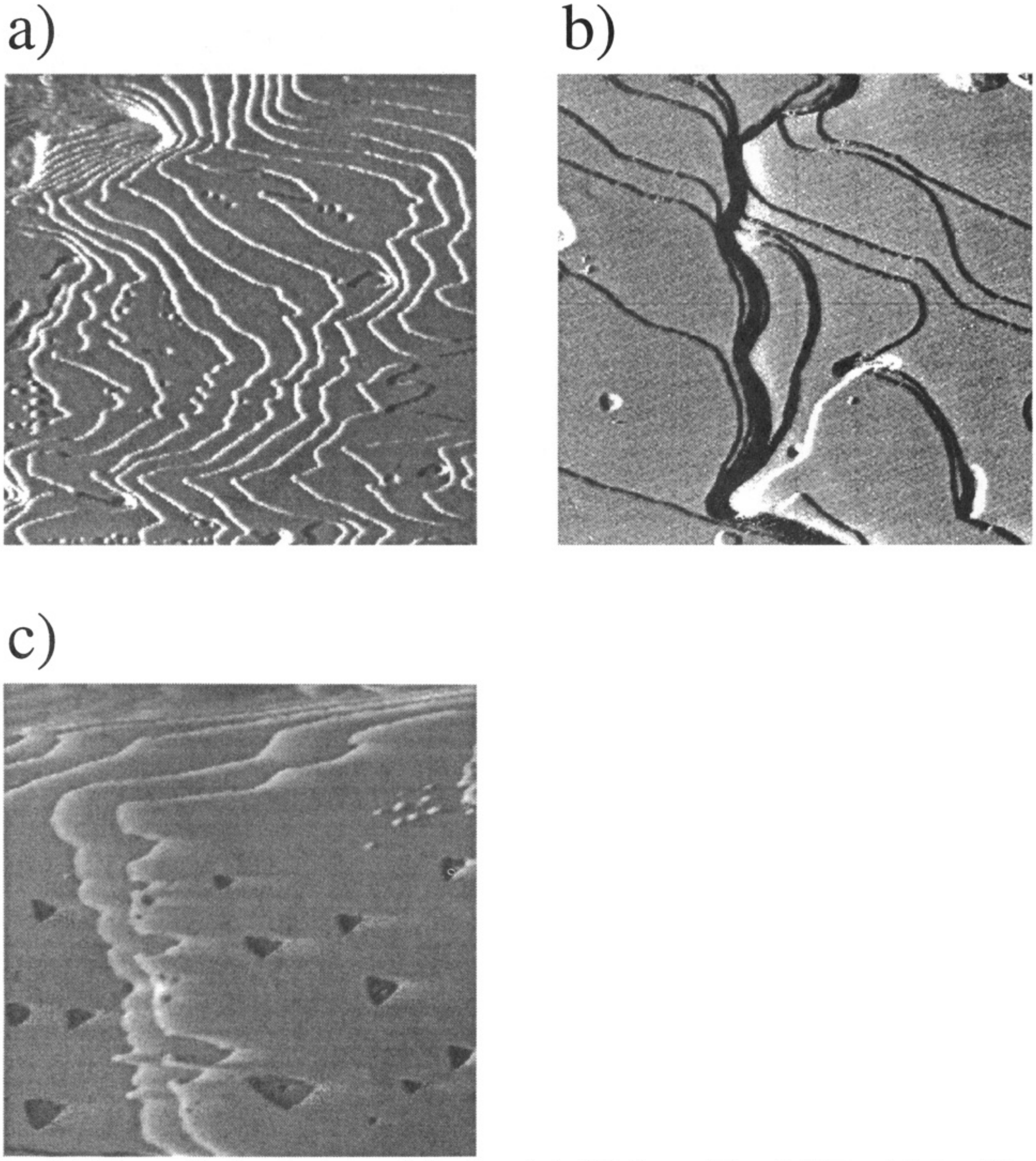

Figure 3. STM images of the thermal evolution and hole coalescence of a SAM of hexanethiol on a Au(111) sample for three different temperatures: (a) 325 K, image 480 nm × 480 nm, $u = 0.6$ V, $i = 0.7$ nA; (b) 345 K, image 480 nm × 480 nm, $u = 0.7$ V, $i = 1$ nA; (c) image taken at 300 K after a short annealing at 345 K, image 400 nm × 400 nm, $u = 50$ mV, $i = 1$ nA. The sample has been immersed for 7 min in a 1 mM hexanethiol/ethanol solution prior to examination.

the propensity of sulfur complexes to mobilize two Ag atoms per sulfur.

In order to study the thermal kinetics and healing of these defects, we have performed STM experiments at elevated sample temperatures. These experiments have been done under controlled atmosphere by continuous flushing of the microscope compartment with dry nitrogen gas. In the present state of the experiment it was not possible to scan the same zone continuously while changing the substrate temperature; nevertheless, the sequence of STM images of Figure 3 was taken on the same sample. In order to avoid thermal drifts during imaging, each STM image has been taken several minutes (typically 30 min) after a temperature change. Figure 3a taken at 325 K gathers several situations in one single STM picture: (i) small holes on terraces are visible in the upper part of the image; (ii) hole coalescence and migration toward terrace edges proceed in the middle left while (iii) holes are about to emerge at the steps in the lower middle part of the image. Although the sample temperature remained constant for minutes, these pictures still change slightly from scan to scan, showing that the system has not reached equilibrium at the time of the examination. Figure 3b has been taken at 345 K, the holes have migrated, and have finally been collected at steps or at surface singularities. Quite generally, the terraces become much larger and more uniform. Although it cannot be proven definitely that the hole coalescence and that migration is solely due to thermal induced effects (a spontaneous time evolution on a large time scale may take place even at room temperature[13] and/or by repeated scanning of the same zone), it remains clear that the process is activated thermally. Upon thermal activation, mass transport proceeds because small vacancy islands diffuse toward steps or coalesce to form bigger holes. Figure 3c shows that on large terraces, big depressions, one Au(111) layer deep can subsist over a large time scale. Since the overall step free-energy tends to be minimized, holes that have diffused toward a step will emerge across it onto the lower terrace leaving behind a torn up contour that will heal to re-form a smooth step again. While holes induced in as prepared gold layers are rarely larger than 4 nm (Figure 2a), the vacancy islands observed after thermal annealing at 345 K are several tens of nanometers wide (Figure 3c). Interestingly this evolution is accompanied by the formation of adsorbed clusters, most probably of gold mercaptides, visible in parts a and c of Figure 3. We verified by Auger analysis that the thiol molecules were still present on the surface after the annealing cycle. This is in accord with the X-ray experiment (ref 9) indicating a substantial increase of the coherence length of $\sqrt{3}$ domains upon annealing up to 363 K but no molecular fragmentation. Auger spectra obtained after sputtering off the thiol layer from the gold surface were identical to the ones obtained on the originally blank Au sample.

Not only do the heating kinetics and the "substrate" nature of the holes become very apparent from the sequence of Figure 3, their quasi-triangular equilibrium shape (formed upon healing) imposed partly by the symmetry of the Au(111) lattice is also very revealing. Based on thermodynamic arguments (Wulff's construction) vacancy islands are expected to adopt a hexagonal shape with ⟨110⟩/{100} and ⟨100⟩/{111} (⟨direction⟩/{microfacet}) island edges. {111} contour edges are usually more stable and therefore give a larger contribution to the perimeter of the deformed hexagon. A qualitative justification of this fact, based on the number of bonds of respective edge atoms can be found in the work of Michely et al.[14] Vacancy islands created by ion bombardment of the Au(111) surface in the vacuum at temperatures under consideration here adopt the hexagonal structure provided islands with edges longer than 10 nm are considered.[14] Although our thiol-induced pits (Figure 3c) are by far larger, they show exclusively triangular shapes with {111} step edges, hinting at a strong unbalance in binding energies of {100} and {111} edge atoms most probably due to the presence of the thiols. While adsorbate-induced effects obviously occur, a more systematic study is necessary to obtain quantitative information.

Certainly an important effect of alkanethiol adsorption on Au is the enhanced mobility they produce on the topmost gold layer. Mass transport allowing substantial rearrangement of surface atoms occurs via hole migration and coalescence. While these effects are clearly absent on gold surfaces in a UHV environment at the temperatures used here (300–350 K), they have been observed to some extent on artificially pitted gold layers exposed to the air.[12] In the case of thiols on gold the increased latteral mobility might be related to the mercaptide complex formation.

In conclusion, while some very recent studies conclude in favor of the depressions in self-assembled thiol monolayers arising from defects in the organic layer packing,[4] or from "electronic" effect,[8] our investigation of hexanethiol and octadecanethiol monolayers on Au(111) and Ag(111) clearly demonstrates the substrate origin of the defects. Upon thermal annealing, the substrate holes migrate and coalesce to form large vacancy islands with triangular equilibrium shape. Upon extensive annealing at 350 K the vacancy islands are annihilated at preexisting substrate steps leaving flat defect-free SAMs.

Noted Added in Proof. After submission of the paper for publication we have become aware of an STM study by McCarley et al. (*Langmuir* **1993**, *9*, 2775) of alkanethiols (n = 5, 15, 17) on Au(111) reaching similar conclusions as presented here.

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