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The Effects of Strain on STM Lithography on HS-ssDNA/Au (111) Surface

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Abstract

Scanning tunneling microscopy (STM) lithography was utilized to investigate a 12-mer HS-ssDNA self-assembled Au (111) surface. Under low sample bias and high tunneling current, the repeated scanning resulted in the growth of nanostripes. The stripe orientation, the stripe width, and the spacer width between adjacent nanostripes were found to be dependent on their relative locations from dislocation points where two adjacent gold terraces overlap. The stripe and the spacer width also vary with the distance from these points. The results indicate that such stripes may reflect the strain distributions and the release pathway along the Au surfaces. The results also suggest that the presence of HS-ssDNA molecules enhances the lithography processes on the gold surface by acting as force transmitters.

Keywords

Scanning Tunneling microscopy; Lithography; DNA; Strain; Self-assembly

1. Introduction

Self-assembly monolayer (SAM) on a metallic surface has been of increasing interest over the past decade because of the wide variety of potential applications, such as molecule electronics [1], biosensors[2], and molecule recognition.[3] The strain field in the metallic surface plays a critical role in the assembly processes [4], especially in the early stage of adsorption. For example, most adsorption is observed to occur at specific sites [5,6]. The surface strain field provides a template for molecule alignment and ordering [5,7]. Inter-molecule reactions can also be moderated by the strain in the substrate surfaces.[8]

On the other hand, it has been reported that the self-assembly process can change the surface stress[9], which can be measured by a micro-cantilever system[10]. It is, however, still very difficult to study the change of local strain at nanometer scales. [9,11]

In this paper, the results of scanning tunneling microscopy (STM) lithography on a HS-ssDNA covered Au (111) surface are reported. The STM lithography produced a nano stripe structure. The stripe orientation, the stripe width, and the spacer width were found to be dependent on

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their relative locations from two dislocation points where two adjacent gold terraces overlap. The stripe and spacer width also vary with the distance from these two points. Results from this work demonstrate that the STM lithography could be used as an efficient tool to visualize the surface strain in SAM covered metallic surfaces. Results also suggest that the presence of HS-ssDNA molecules enhances the STM lithography on gold surface. The growth mechanism of the gold stripes with the presence of a HS-ssDNA layer is also discussed.

2. Experimental Section

2.1 Materials

The thiol-derivated 12-mer probes oligonucleotide (HS-ssDNA) solution, SH-(CH₂)₆ 5' AAATCGAAGATC3' was obtained from SynGen, Inc. (San Carlos, CA) and was dissolved in molecular biology level water. 1-Octanethiol (C8m) and all other reagents were purchased from Sigma-Aldrich (St. Louis, MO).

2.2 Solution preparation

A phosphate buffer 1 M K₂HPO₄ + KH₂PO₄ (pH of 6.7) was made with double distilled water (Millipore, MA). A 1-octanethiol solution was made from toluene with 1mM concentration.

2.3 Au (111) substrates

Substrates used for STM studies are ~ 200 nm gold evaporated on fresh-peeled mica substrates; these were obtained from Agilent AFM (Tempe, AZ). The substrates were annealed in a hydrogen flame for 90 seconds immediately before use.

2.4 Instrumentation

A PicoPlus system from Agilent AFM (Tempe, AZ) was used for STM imaging and lithography. The STM tips were made by etching Pt_{0.8}Ir_{0.2} wires. A sample chamber was used to provide an argon environment. An STM scanner with a maximum scan range of 1.5 μm was used.

2.5 Immobilization of the probe HS-ssDNA

The hydrogen flame annealed gold substrate was immersed in 1.0 μM of probe HS-ssDNA in a 1.0 M potassium phosphate buffer for 6 hours at 4°C. The gold substrate was then removed from the solution, rinsed thoroughly with distilled water and dried in an argon flowing stream.

2.6 Preparation of C8m sample

The C8m sample was prepared by immersing hydrogen flame annealed gold substrate in a 1mM octanethiol solution in toluene for 24 hours, after which the sample was thoroughly rinsed with toluene and dried in a flowing argon environment.

2.7 STM imaging and lithography

The STM imaging was performed in an argon atmosphere in the constant current mode. The STM lithography was realized by repetitively scanning the same area under fixed imaging parameters, i.e., sample bias and tunneling current setpoint. Typical lithography size is 200×200nm. The sample bias was varied from -1V to -100mV with tunneling current changing from 50pA to 1nA. Unless stated, the images were acquired during each lithography scan with the same parameters when the tip was scanning from left to right. The scan rate was kept at 2.7~3.1 lines/s.

3. Results and Discussion

3.1 Growth of nanostripes—sample bias and tunneling current effect

Typical STM images (200nm×200nm) of a 12-mer HS-ssDNA sample assembled for 6 hours on gold (111) substrates are shown in Figure 1. The Z ranges in all images are 1.7nm. The images in Figures 1a and 1b were obtained by using a −0.5V sample bias and a 50pA tunneling current setpoint at the 1st (a) and the 50th (b) scan, respectively. Although the image in Figure 1b has a slight drift from the image in Figure 1a, the topography features in both images are similar in terms of terrace shape and noise levels. Small dots with a typical height of a few angstroms scatter around the surface.

The cross-section profiles, displayed as dashed lines in images a, b, c, and d, are labeled numerically “1” through “6”. Profiles 1 and 2 show 3.5–4 Å step heights; these are larger than the single gold layer height of 2.5 Å. The reason for observed larger gold layer height unclear but could be attributed to the amorphous status of the HS-ssDNA molecules coated on the gold surface.

The image in Figure 1c was acquired at the 1st scan using the same sample bias (−0.5 V) but with a higher tunneling current setpoint of 500pA. Slight drift is also observed in this image. The features in Figure 1c are similar to those in Figures 1a and 1b. The image shown in Figure 1d was obtained at the 56th repeated scan using −0.5V and 500pA. This image shows significant differences from other three. The left half of the image in Figure 1d looks much smoother, while on the right side some bright spots are clearly seen. The two large pits in Figure 1c (labeled 3 and 4) are broadened in Figure 1d (5 and 6) after 56 scans, as shown in cross-section profiles 3–6. This broadening is most likely related to the repeated scans with increased current setpoint 500pA.

The bright dots shown on the right half of Figure 1d are mainly round in shape with an average diameter of 6.68nm and an apparent height of 0.96nm. These results seem to indicate that the HS-ssDNA molecules in the left side of Figure 1d (alone or with gold atoms from the substrate) are pushed to the right by the STM tip during the left-to-right scanning.

Figure 2 shows sequential STM images (200nm×200nm) obtained with −100mV sample bias and 1nA current setpoint at the 1st (Fig. 2a), the 7th (Fig. 2b), and the 15th scans (Fig. 2c). Compared to those used in Figure 1, the sample bias used in Figure 2 is reduced and the tunneling current is increased. Generally this will result in a decrease in the tip-sample separation because the tunneling current is exponential to tip-sample separation and proportional to sample bias, provided that the charge carrier's population density of the sample and the tip does not change over the carrier's energy. Numerals “i”, “ii”, “iii”, and “iv” (Figure 2) indicate four regions to be discussed. “Terrace-A” marks the central top terrace. “Terrace-B” marks the terrace beneath Terrace-A.

One can easily observe the appearance of two parallel step-edges at the left and bottom edges of Terrace-A in Figure 2a. This is attributed to the double-tip effect.[12] The STM images produced by a double-tip or multi-tip will show duplicate features, e.g., pits, dots, and step edges. Note also that neither the right terrace edges in Figure 2a (close to location ii), nor the teeth-like features marked by the green arrow are duplicated in Figure 2a.

For simplicity, the double-tip geography is schematically illustrated in Figure 3 (the image therein is Figure 2a). The line profiles (a), (b), and (e) show the step-down scanning direction, while (c) and (d) indicate the step-up scanning direction. These images were taken with the STM tip scanning from left to right, and similar double tip effects are expected when images are taken from right to left. The scanning direction does not affect the double tip effects due

to the geometry of the tip end shown in Fig 3-(f). The double steps in (c) and (d) are 0.14nm and 0.1nm high, respectively. In a contrast, the step height at the right terrace edges (e.g., (a) and (b)) is about 0.24nm, which is consistent with the actual single step height of 0.25nm on Au(111) surfaces. This consistence is a typical example that imaged surface feature would reflect the tip morphology.[12] From the line profiles (a-e) in Figure 3, the double-tip geography can be explained by a schematic illustration as shown in Figure 3(f). This figure indicates a major tip (left, the actual STM tip) and a minor tip (right) that is 6 nm away from the major tip and is about 0.1 nm–.14 nm shorter than the major tip. These numbers can be estimated from the line profiles (c) and (d) in Figure 3.

The scanning process described below demonstrates the reason the duplicated step is only observed at the left and bottom of terrace edges. When a STM tip scans over the surface, the closest point of the tip to the surface dominates the tunneling current. In the cases of (c) and (d) in Fig. 3, when a double tip with a geography as illustrated in Fig. 3(f) reaches the left edges of Terrace-A, the minor tip touches the surface first, which dominates the tunneling current and the feedback circuit drives the double tip to move away from the surface in order to keep the tunneling current at the setpoint. The left step edge of Terrace-A is then first imaged by the minor tip. When the scan continues from left to right, the major tip then touches the same left edge of the terrace. Because the major tip is longer than the minor tip, the tunneling current is then dominated by the major tip and the feedback circuit retracts the double tip once again to maintain the tunneling current at setpoint, which creates the second step in the image. In the step-down scanning ((a) and (b)), the tunneling current via the major tip (closer to the surface) would dominate the switch from imaging the top terrace, across the step edge, and then the lower terrace (scanning from the left to the right). Therefore the surface will be imaged only by the major tip. In this case, no duplicate features would be observed.

This double-tip effect can also be distinguished in Figure 2b (the image from the 7th scan), but not in Figure 2c (the image from the 15th scan). The presence of the double-tip effect can be attributed to the physical interaction between the STM tip and the sample surface. Gold atoms or HS-ssDNA molecules could be transferred from the sample surface and attached to the original STM tip. These attachments may result in the generation of another tunneling current responding pathway (the minor tip in Figure 3(f)).

As the number of scans increases (from 1st to 15th), tooth-like features begin to appear and are elongated into stripes in regions (i)-(iv). This change can be clearly seen in the sequential STM images (Figure 2). The variation of the stripe length (averaged from the length of the longest four stripes in region (iv)) versus the number of scans is shown as the solid black squares (left y-axis) in Figure 2d. The stripe length increases almost linearly, with an estimated growth rate of 4.9nm/s.

3.2 Characterization of the nanostripes

The stripe widths, represented by the red hollow circles in Fig. 2d with reference to the right y-axis (data are averaged from the widths of the longest four stripes in region iv), remain relatively unchanged, showing about 6–8 nm at the initial stage (from first to the 10th scan), dropping to 2–3nm at the 11th scan, and finally reaching at stable value of 2–3nm starting from the 14th scan. The initial 6–8nm apparent stripe width probably results from a mixture of the real nanostripes and their duplicated features produced by the double-tip. Subsequently, the sharp jump from 6–8nm to 2–3nm from the 11th scan can be attributed to the appearance and disappearance of the double-tip effect, which are visible in the STM images (not shown). An aspect ratio of 46 (defined as stripe length/stripe width) can be estimated from the longest stripes in region (iv) from the 15th scan (Fig. 2c). The stripe width in regions (i) through (iii) was 2–4 nm, which will be discussed in more details in the following text. Similar aspect ratios

of 11, 12.7, and 23.5 can be estimated from the longest stripes at regions (i), (ii) and (iii) from the same image (Fig. 2c).

Figure 2d shows the variation of spacer widths between adjacent stripes in region (iv) as a function of number of scans (blue solid triangle, right y-axis). The stable spacer width from the 15th scan in region (iv) is measured as 6–8nm. Although the spacer width of 6–8nm and the stripe width of 2–3nm are close to the distance between the major and the minor tip as shown in Figure 3, we do not believe that the stripe structures in Figure 2c are artifacts of the double tip because of the significant observations below.

First, the double tip effect is known to cause duplicate features. There are no duplicated features in Figure 2c when considering the stripe length, the stripe width, and the spacer width. Second, the stripes in regions (iii) and (iv) are found to orient $2.3\text{--}3^\circ$ from the horizontal line. The stripes in regions (i) and (ii) have a slightly larger angle of $10\text{--}12^\circ$ ver the horizontal line. Third, these stripes are pointing in opposite directions. For example, the stripe orientation in regions (i) and (iii) is opposite to that in regions (ii) and (iv). As discussed above, the duplicated features should only appear at the left side of the terrace due to the double-tip geometry and the scan direction. Fourth, the growth of such stripes occurs at both ends of each stripe, i.e., both ends grow longer with increasing number of scans. The length of the stripes can be as long as 100nm. It is highly unlikely that a double-tip effect to grow in such a continuous manner.

Cross-section profile analysis reveals the heights of these stripes to be approximately $2.5\text{\AA}$, the typical single gold atomic layer height, suggesting the strips consist of a single gold layer. Additionally, the spacer areas between two adjacent gold stripes have a preferred angle of 120° (or expressed in its supplementary angle, 60°), which can be attributed to the three-axial symmetry. A magnified in view of region (iii) from Figure 2c is shown in Figure 4. The angles shown in the graph are measured along the dashed white lines. These analyses suggest that the observed nanostructures are mostly likely formed in the gold substrates.

To test the reproducibility of such nanostructures, STM lithography using the same or similar ($-mV$ and $2nA$) conditions was performed on other locations of the same sample and on other HS-ssDNA/Au samples. Similar nanostructures with similar widths were also observed (Please refer to the supplementary data).

Other researchers have observed similar gold stripes (also called gold fingers) forming on bare gold surfaces by directly manipulating the gold surface.[13–18] Compared to these reported results, the data presented in this paper show both similarities and differences. The similarities are, for example, the stripe height and length, the growth behaviors, and the independence of the stripe orientation from the original step edge and the STM fast-scan direction. Judging from these similarities and considering that fact that this research utilized HS-ssDNA coated gold surfaces, the authors conclude that the stripes observed in these results are also formed in the gold substrate instead of in the HS-ssDNA self assembly layers.

The first major difference between the reported gold stripes formed on bare gold surface and the stripes in this work is the stripe orientations. The previously observed stripes were all parallel and pointing only in one direction. Initially, the stripe direction was proposed to be the same as the discommensuration lines of the $22 \times \sqrt{3}$ reconstruction in gold (111) surfaces. [15] Recently, Guo et al.[16] obtained clear images of gold stripes with distinguishable discommensuration lines. They concluded that the stripe direction is not same as that of the discommensuration lines, but one of the $\langle 110 \rangle$ directions.[16]

In the results presented in this paper, the stripes are roughly parallel within each region, while the stripe orientation angle differs between regions. The measured angle of the nano stripes in regions (i) and (ii) varied about $8\text{--}10$ degrees from that in regions (iii) and (iv). This difference

in the growth directions (or growth angle) of the gold nano-stripes suggests that the atomic arrangements on the top surface are different from those underlying ones.

A second major difference is the stripe width and the interval between the adjacent stripes. In previous studies,[13–18] the width of the gold stripes was reported to be about 3–8 nm, and the width of the interval space between neighboring stripes was either 6.5 nm or 13 nm, which was assumed to be the same as or twice the width of the reconstruction domains, respectively. [15,16] In the results presented here, the stripe width is approximately 2–3 nm, which is smaller than those previously reported. The width of the interval space between two adjacent stripes in these results varies from 3 to 10 nm in three different regions. The stripe width and interval width are believed to be correlated to the stress field in the Au (111) surface due to the $22 \times \sqrt{3}$ surface reconstruction.[16–18] Therefore, the different stripe and interval widths in the HS-ssDNA coated Au (111) samples would suggest that the gold surface may have a different strain field after being coated with HS-ssDNA layers.

3.3 Origin of the nanostripes—strain effect?

Although no discommensuration lines are resolved in the experiments documented here, other features observed in the STM images could help to evaluate the strain in HS-ssDNA coated gold surfaces.

Figure 5a is the same image as that in Figure 2a. Terrace-A marks the same terrace as in Figure 2. Terrace-C marks the one on the upper left which is one layer higher than Terrace-A. There are two distortion areas as marked by the dashed green circles in Figure 5a (Point-A and Point-B). It is notable that the observed stripes in Figure 2c are surrounding these two areas. Such terrace overlap along with formation of gold stripes nearby was also observed previously on bare (111) surfaces of gold.[16] The overlap points are considered “Stress points” (namely, Point-A and Point-B).

The strain may project in different directions as indicated by the dashed cyan and blue arrows in Figure 5a. The stress amount, field strength, and strain projecting direction can be visualized by measuring the step-height changes along these two directions. In Terrace-C, two starting points, A and B, are selected at random in the two overlap regions (Figure 5a), respectively. From there, zero step height and maximum distortion (stress) are expected.

As shown in Figures 5b and 5c, the step height increases from zero (where the two terraces overlap) to 2.5 Å (the single gold layer height) starting from point-A along the cyan arrow (5b) and from point-B along the blue arrow (5c), respectively. Within a typical 20 nm range, the step-height changes from zero to full single gold layer height. Both curves show an initial linear increase and then a slower change up to the height of single gold layer. The slopes illustrated by the dashed lines in Figs. 5b and 5c yield tilt angles of 2.5° and 1.7°, respectively.

The similar atomic arrangement suggests that the nature of strain near these points has common factors that influence the detachment of gold atoms under the local electric field of an STM tip. The nano-stripes in regions (i) and (ii) (Figure 2c), which have a larger orientation angle versus the horizontal line, could be attributed to the strain fields originating from these two points, A and B in Figure 5. It is worth noting that the stripes in regions (i) and (ii) (Figure 2c) are mainly produced in Terrace-C. The measured angle of the nano stripes in Terrace-C varied about 8–10 degrees from those in Terrace-A. This stripe orientation difference may reveal the different strain release directions between the upper (Terrace-C) and the lower terrace (Terrace-A).

The arrangement of atoms on the same plane with the dislocation points A and B can be mapped out through the detailed analysis of this STM picture and will be published elsewhere. The

nature of stress in nanostripes on Au (111) the surface of bare gold is due to incommensurate arrangement of atoms. The results of this research show that the different nature of stress, e.g., the stress due to terrace bending, may yield nano stripes with different stripe width, length, and orientation angle.

Moreover, the thinning progressed significantly in regions (iii) and (iv), but not in regions (i) and (ii), as is clearly shown in Figure 2b and 2c. This thinning process seems dependent upon strain field, as shown in Figure 5, where points A and B indicate originating spots of dislocation with a high strain field similar to the results observed by Yin et al.[17, 18] It is interesting to note that no stripes are formed along the terrace edge between the two stress points.

Figure 6a shows the same STM image as in Fig. 2c. The dashed green cycles mark the two stress points as defined above. The four cross-section profiles in Fig. 6b are made along the dashed arrows and are shifted vertically to separate from each other. The stripe (square) and spacer (circle) width in Fig. 6c was measured at the half-maximum stripe height as a function of relative distance from the stress points. The lines in the insets are visual guides. “Terrace-A” and “Terrace-C” mark the lower and the upper terraces, respectively.

The stripe width was found to decrease with the relative distance from the stress point. This decrease is more pronounced in regions (i) and (ii) than in regions (iii) and (iv). The stripes in regions (i) and (ii) are both located in Terrace-C, the upper terrace of the stress point, while those in regions (iii) and (iv) are mainly in Terrace-A, the lower terrace of the stress points. The terrace difference may account for the different stripe width variation behaviors. If this conclusion is correct, a logical deduction could be that the stress points have more influences on the stripes formed in the upper terrace than on those in the lower one. This may also suggest that the strain release is more significant in the upper terrace, which is reasonable because the lower terrace is restricted by its under-layers and thus has less distortion flexibility.

Compared to the stripe width, the spacer width shows different behaviors. In regions (ii) and (iii), the spacer width increases with the increasing distance from the stress points, suggesting relaxed strain fields with distance. However, the opposite variation is seen in regions (i) and (iv). A careful review of the terrace geometry revealed that this difference can be interpreted by the terrace's neighboring structures.

Figure 6a shows two major strain relaxation directions. One is along the stripes, and the relaxation is represented by elongation of the stripes. The other is perpendicular to the stripe orientation, and the relaxation is represented by the changes of stripe width and spacer width. The along stripe relaxation is similar for all regions, while the perpendicular relaxation is different.

As indicated by the arrows, regions (ii) and (iii) both have open step edges in the direction perpendicular to the stripes that act as strain release ports. However, such perpendicular release ports are not available in regions (i) and (iv) where stripes are formed inside the large terraces; in such cases the perpendicular relaxations are circumscribed. As evidence, the spacer widths in regions (i) and (iv) have maximum value in the middle, indicating that the far end spacer width is restricted by the terraces.

To the best of our knowledge, there are no reports of gold stripes observed in a SAM coated gold surface. The lithography conditions used here are lower than those applied on bare gold. [16] Results from present HS-ssDNA coated surfaces suggest that the DNA layers seem to enhance the growth of gold nano stripes.

3.4 Nanostripe growth mechanism—enhanced lithography

Different mechanisms have been proposed to explain the formation of gold stripes on bare gold surfaces. Emch et al.[13] attributed the formation of gold stripes to faster diffusion speed along the long axes of the stripes. Kim et al.[15] concluded that the Au atom diffusion was first triggered by pulsed voltage applied via the STM tip and that the growth of stripes resulted from a field gradient effect due to tip-sample interaction. Guo et al.[16] proposed that the high local electric field between the STM tip and the gold surface moved the gold atoms from their original locations and reassembled them along the stripes. They excluded the effects of bonding (between the tip and the gold surface) and mechanical scratching. Guo et al claimed that the modification on gold surfaces only occurred with a sample bias higher than 1V.

To test whether the same scanning conditions used in producing gold stripes in HS-ssDNA coated surfaces would generate such structures on bare gold surface, a control experiment on a bare gold surface was also conducted using the same scanning parameters, i.e., -100mV bias and 1nA current setpoint. The STM images ($500\times 500\text{nm}$) obtained on the 1st and 73rd scans (Figures 7a and 7b, respectively) exhibit no observable differences. Therefore, the stripes observed in Figure 2 suggest that the DNA assembly layer enhanced the manipulation effect on the gold surface.

In order to further identify the role of the HS-ssDNA molecules in generating gold nano-stripes, another control experiment was conducted on n-alkanethiol SAM modified gold (111) surface [19–21] using the same scanning parameters, i.e., -100mV bias and 1nA current. The 1-Octanethiol (C8m) SAM on Au (111) surface was chosen for this control experiment. The repeated scanning on C8m SAM was performed in a $200\text{nm}\times 200\text{nm}$ area. To emphasize the differences in the STM images before and after repeated scans, the STM images from C8m were collected in a larger range, $500\times 500\text{nm}$, using normal imaging parameters, -0.5V bias and 50pA current setpoint. The STM images acquired on the 2nd scan and after 172 repeated scans are shown in Figures 7c and 7d, respectively. The STM image of fresh C8m SAM surface on gold (111) consists of atomic smooth terraces with clear pits and sharp steps (Figure 7c). The repeated scan was initialized within the range marked by the blue dashed square in Figure 7c. Due to sample drifting, the most significant feature after STM lithograph etching is the rectangular area as marked in Fig. 7d, as marked by the red rectangle with a higher edge at its right side.

Cross-section profile analysis (data not shown) indicates that the area inside this range is lower than those outside. Apparently, materials (C8m molecules, or C8m molecules with bonded gold atoms) are removed from this range and piled up at the right edge of the scan areas as reported previously.[19–21] In addition to the rectangular region, the pits and island outside this range are also modified by repeated scans. No stripe-like features were observed. Different lithography conditions have also been tested on the C8m SAM sample (data not shown), but no stripe structures were observed in those tests. This result is consistent with other reports on STM lithography n-alkanethiol SAMs. [19–21] Therefore, the authors conclude that the lithography mechanism in the results herein reported on HS-ssDNA coated gold surfaces is also unique from that in n-alkanethiol SAM on gold surfaces.

In the analyses presented in this paper, the formation of gold stripes on the HS-ssDNA coated gold surfaces is only observed under the lowest bias and highest tunneling current among the three conditions used. The lower bias and higher tunneling current indicate a shorter tip-sample separation. This suggests that mechanical scratch could dominate the lithography process in HS-ssDNA coated gold surfaces. This removal mechanism on HS-ssDNA coated gold surface is shown in Figure 8. Under the scanning conditions of -100mV sample bias and 1nA current setpoint, the STM tip may penetrate the HS-ssDNA SAM to reach and maintain the current setpoint during scanning. Due to the amorphous assembly of HS-ssDNA molecules as revealed

by the STM images in Figure 1, the inter-molecule binding between the HS-ssDNA molecules is much weaker than that between Alkanethiol molecules. Therefore, the HS-ssDNA molecules are more easily removed by the STM tip via mechanical scratching. Subsequently, the motion of the STM tip can drag the HS-ssDNA molecules away from the gold substrate surface. The movement of the HS-ssDNA molecule causes extraction of the first layer of gold atoms that are bonded to the sulfur atoms (on one end of the HS-ssDNA molecules) (Figure 8a). In other words, the lateral drag force from the STM tip's motion during repeated scanning is transferred via the HS-ssDNA molecule to the gold atom on the substrate. Similar removal of gold atoms via thiol molecules has been previously observed by Keel et al.[22] during STM lithography on a dodecanethiol SAM (C12m) modified Au (111) surfaces. As the scans are repeated, more and more gold atoms (from the first gold layer) are removed (Figure 8b and 8c). Such removal of gold atoms is not isotropic; the gold atoms in some regions are removed while some in other regions are left, forming the stripe structure. Considering the fast scan speed of 2~3 lines/s, the STM tip may crash into the terrace before the feedback circuit can pull it away while it approaches from a lower terrace. This crash effect, which is not illustrated here, may play an important role in lithography at the ascent terrace edges.

There could be several reasons no stripes were observed in n-alkanethiol SAM on gold (111) [19–21]. First, the Alkanethiol SAM is so condensed that it would be difficult for the STM tip to lift up individual Alkanethiol molecules attached to gold atoms. In another words, the condensed Alkanethiol SAM acts as a strain barrier that blocks manipulation from the tip to the gold surface. The observed gold stripes in the results presented here may imply that HS-ssDNA molecules can efficiently transfer the lateral drag force from the STM tip's motion to the gold atoms and could therefore enhance the lithography on the gold substrate. The chemistry of surface chemical modifications (e.g., DNA) is believed to play critical role in the change of STM lithography behaviors on these modified surfaces. It would be valuable to investigate the effects of different functional groups of these coated (bio)molecules on the formation of nanostructured features on these modified substrates; the results could lead to the next generation of bionanoelectronics.

CONCLUSION

The authors investigated STM lithography on HS-ssDNA self-assemble monolayer coated Au (111) substrate and observed fabrication of nano-stripes after a few scans under -100mV sample bias and 1nA tunneling current. The stripe orientation, the stripe width, and the spacer width were found to be dependent upon their relative locations from two dislocation points where two adjacent gold terraces overlap. The stripe and spacer width also varied with the distance from these two points. Results suggest that such stripes visualize the strain distributions and the release directions in the Au surfaces. Results also suggest that the presence of HS-ssDNA molecules enhances the lithograph processes on the gold surface. In the proposed lithography mechanism, the HS-ssDNA molecules play the role of transferring the drag force from the STM tip's motion to the gold atoms and enhancing the manipulation effect on gold surfaces.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

STM images (200×200 nm) taken on a 12-mer HS-ssDNA assembled for 6 hrs on Au (111) surface. The images (a) and (b) are collected at 1st and 50th scans, respectively, under bias -0.5 V and tunneling current 50 pA. Images (c) and (d) are acquired at 1st and 56th scans, respectively, under bias -0.5 V and tunneling current 500 pA, respectively. Z ranges in all images are 1.7 nm. The cross-section profiles 1–6 correspond to the marked locations 1–6 in images (a)–(d).

Figure 2.

Sequential STM images obtained at the 1st (a), 7th (b), and the 15th (c) scans under $-100\text{mV}/1\text{nA}$. The stripe length (■), width (○), and inter-stripe space width (▲) at location (iv) versus the number of scans (d). Scale bar: 50 nm. Z ranges in all images are 0.8nm.

Figure 3.

Same STM image as in Figure 2a. Line profiles across the step edges on the surface. Step-up edges such as line c and d show double heights of $\sim 0.1\text{ nm} \sim 0.14\text{ nm}$. The line profiles suggest that the tip is the double-tip that has one side lower than the other one, as shown in (f).

Figure 4. Magnified STM image from the region (iii) in Figure 2c. The angles are measured along the dashed lines. Z range: 0.5nm.

Figure 5.

STM image in Fig. 2a (a), step-height versus relative relax-distance curve starting from Point-A (b) and Point-B (c) along the cyan and blue arrows, respectively. Z range: 0.8 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article).

Figure 6.

STM image (a) same as Fig. 2c, cross-section profile (b) along the dashed lines in regions (i) to (iv), the stripe width (c) and inter-stripe space width (d) as a function of relative distance from the stress points. The lines in (b) and (c) are visual guides.

Figure 7. STM images (200×200nm) of bare gold surface acquired at the 1st (a) and the 73th (b) scan, STM images (500×500nm) of C8m assembled for 24hrs taken at the 2nd scan (c) and after 172 repeated scans in a 200×200nm range (d). Scale bar: 100 nm. Z ranges in all images are 0.6nm

Figure 8. Schematic diagram of three stages (a, b, c) during STM lithography on HS-ssDNA/Au (111). The tip-sample separation is just a visual guide.