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Spurious dangling bond formation during atomically precise hydrogen depassivation lithography on Si(100): The role of liberated hydrogen

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The production of spurious dangling bonds during the hydrogen depassivation lithography process on Si(100)-H is studied. It is shown that the number of spurious dangling bonds produced depends on the size of the primary pattern on the surface, not on the electron dose, indicating that the spurious dangling bonds are formed via an interaction of the liberated hydrogen with the surface. It is also shown that repassivation may occur if hydrogen depassivation lithography is performed near an already patterned area. Finally, it is argued that the product of the interaction is a single dangling bond next to a monohydride silicon on a silicon dimer, with a reaction probability much in excess of that previously observed. © *2014 American Vacuum Society*.
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I. INTRODUCTION

Hydrogen depassivation lithography (HDL) from Si(100)-H using a scanning tunneling microscope (STM) promises to revolutionize the precision of manufacturing,[1] allowing the templating of surfaces so that chemically reactive areas can be formed with precision down to the single atom scale. HDL has already been shown to be a critical component of patterned atomic layer epitaxy,[2] template formation for phosphorus doping for device fabrication,[3] and many other patterned surface functionalization processes.[4,5] Critical to creating these precise templates is a fundamental understanding of the removal of the hydrogen passivation layer to produce areas of dangling bonds (DBs) where—and only where—desired.

The HDL process is similar to e-beam lithography in several ways. Both techniques provide electrons to modify a surface, and the spot size can be varied in both cases. However, the fundamental physics of the two processes vary in important ways. Proximity effects in e-beam lithography such as backscattered electrons[6] are absent in HDL. Since HDL is typically performed below 10 V, secondary electron production and backscattering are minimized, eliminating these e-beam lithography proximity effects, although backscattered electron effects have been observed for HDL above 20 V.[7,8] However, the presence of the tip does introduce an additional proximity effect in HDL not typically seen in e-beam lithography: production of DBs due to the presence of hydrogen atoms nominally liberated from the surface. This is a resist-induced proximity effect.

A general consensus for the mechanism of hydrogen depassivation includes either a direct excitation of the Si-H stretch to an antibonding state or a multielectron ladder-climbing process, depending upon the incoming electron energy.[9,10] For voltages above ~6 V, the HDL spot is typically similar to a Gaussian distribution with a region in the center with the greatest HDL surrounded by regions of less HDL. At high enough electron doses the center of the spot may become fully exposed so that all of the hydrogen is removed, but above 6 V, there is still generally a halo of partially exposed areas.[7,11] Since this linewidth depends upon electron dose, much of the halo can be attributed to electron stimulation from the STM tip.[11] However, at HDL voltages below approximately 4.5 V and sufficiently high current, the HDL spot size becomes atomically precise and above a threshold somewhat independent of electron dose.[12] This work shows the formation of spurious DBs formation well outside the primary patterned area during these low voltage processes,[3,11–14] an effect that is difficult to observe at higher voltages due to the tails of the high V spot. While much study has been devoted to the role of electron energy transfer in HDL, little has been devoted to the nature of the dissociative reaction products (liberated H) as described here.

This text shows that areas of spurious DBs outside the pattern during low voltage HDL originate primarily from atomic hydrogen, which has been liberated from the surface during HDL, using a process and system already described.[15] In other words, the number of these spurious DBs depends upon the number of hydrogen atoms leaving the surface and *not* on the total electron dose. It is further shown that removing H from an area near an already depassivated region can in fact *repassivate* the surface. Repeated experiments show that up to an average of 10% of departing hydrogen atoms further modify the surface, depending upon the STM tip used for HDL. Finally, a morphological comparison of a dihydride dimer with a monohydride dimer will help elucidate the nature of the spurious DBs.

II. EXPERIMENTAL AND RESULTS

It is well established that HDL at certain voltages produces isolated DBs either due to excitation from primary[9] or backscattered[7] electrons, so the number of spurious DBs can

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in some instances depend on this mechanism. To test the direct electron excitation role in spurious DB formation for low voltage HDL, a dose dependent study of the spurious DB density was performed. Since the presence of the H resist is binary with each H atom either being present or not, after a saturating electron dose is applied, further exposure can remove no more H from the desired pattern area. This permits a comparison where all primary patterns are produced using over-exposed conditions. As such, all primary patterns were fully exposed and contained 80 DBs. Figure 1(a) shows a typical image of an area after HDL using 4 V sample bias and 4 nA tunnel current. The two patterns on the left were patterned with a total electron dose of 31 nC, and the two on the right had a total electron dose of 125 nC. To analyze, DBs that were not apparent in the "before" image (not shown) and were *not* contiguous with a pattern were counted. Those on the left half of the image were attributed to the low-dose patterning and those on the right were attributed to the high-dose patterning. After 11 trials, the average numbers of DBs were compiled; the results are shown in Fig. 1(b). For a 31 nC pattern dose, 10.8 DBs on average were observed, and for a 125 nC pattern dose 11.6 new DBs on average were observed. This supports the conclusion that for low-voltage HDL the primary source of spurious DBs is not direct electron stimulation.

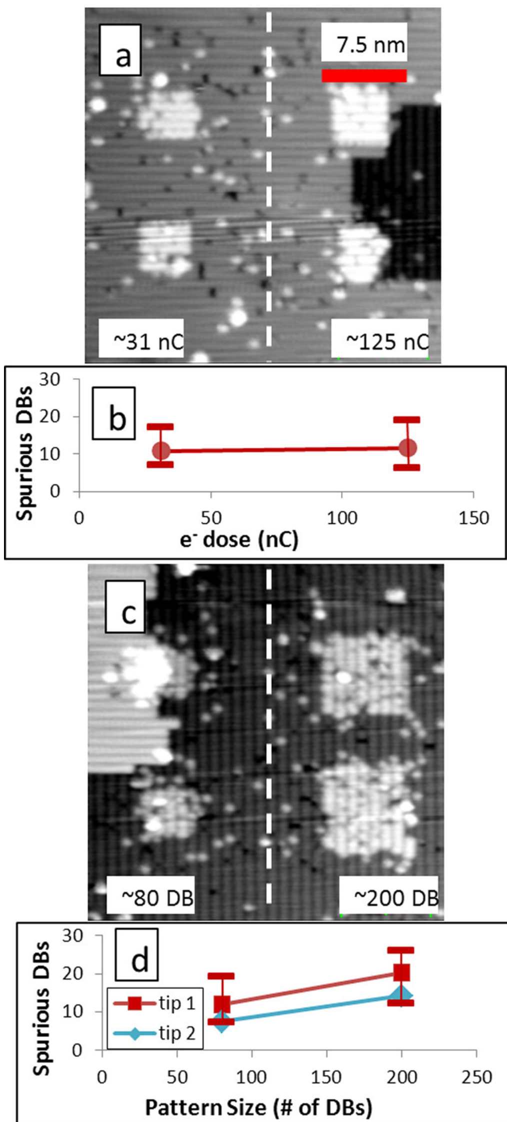

FIG. 1. (Color online) Dose and pattern size dependence of spurious DB production. (a) STM image after HDL with constant pattern size, variable dose. Doses for the left and right sides are indicated. (b) Average number of spurious DBs as a function of electron dose for 80 DB patterns. The range of DB counts for each trial is included. (c) STM image after HDL with constant dose, variable pattern size. (d) Average number of spurious DBs as a function of pattern size for two separate tips. The range of DB counts over all trials is included for tip 1.

To study what other possible mechanisms are at play besides direct electron excitation, a comparison was made of patterns of different sizes. Figure 1(c) shows a typical image where both the left and right side patterns were produced with 4 V sample bias, 4 nA current, and 125 nC electron dose. However, the patterns on the left side of the image consist of about 80 DBs, while those on the right side consist of about 200 DBs. Since all patterns were created with over-saturating conditions, the variation in pattern size was achieved by changing the tip's path length while maintaining the same total patterning time and current. For the same tip as above, after seven trials, the average number of new spurious DBs on the left and right sides of the images were 12.0 DBs and 20.2 DBs, respectively, which is compiled into Fig. 1(d). This was repeated using a different tip, with a similar trend but lower overall DB production. The ratio of the number of spurious DBs on the right versus the left is shown to be 1.68 and 1.83, indicating that there is a dependence of the number of spurious DBs on the size of the HDL pattern. These ratios are slightly less than the ratio of pattern sizes, but they may be underestimated for two reasons: the effective background area used for counting (i.e., total area minus the patterned area) is less for the larger patterns than for the smaller patterns, and there is a possibility that some DBs from the patterns on the right side were formed on the left side, driving the ratio toward 1. See Table I for a summary of these results.

We also investigated the effect of depassivation near an already depassivated area. Figure 2(a) shows a control pattern that was written using 4 V, 4 nA, and the same dose density as the left side of Fig. 1(a). The pattern is largely depassivated with some spurious DBs on the background. Next, two nearby areas were patterned using the same conditions. Figure 2(b) clearly shows a significant number of dark spots in the center control pattern, supporting the conclusion that *hydrogen moved onto the control pattern*, strengthening the conclusion that the spurious DBs result from liberated hydrogen.

TABLE I. Number of spurious DBs vs pattern size and electron dose.

		80 DB pattern	200 DB pattern
Electron dose (nC)	31 nC	11	Subsaturating dose[a]
	125 nC	12	21

[a]Since the total dose was subsaturating, the number of liberated H was inconsistent and thus not compiled.

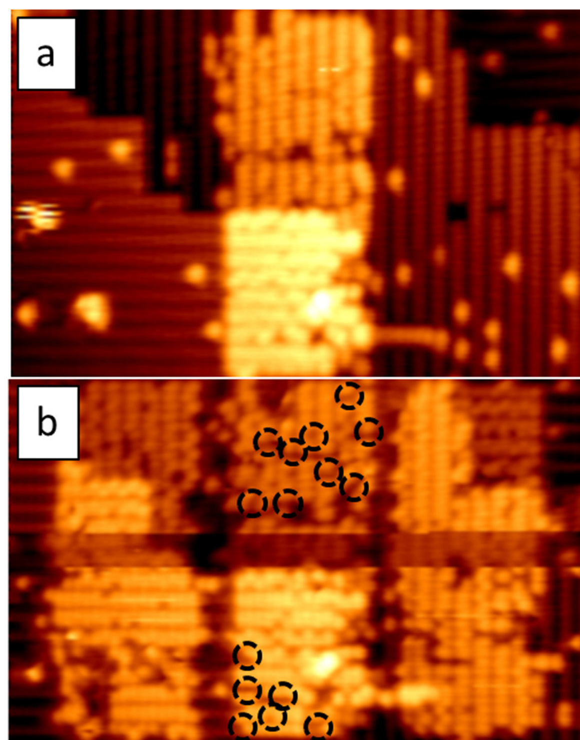

FIG. 2. (Color online) Spurious repassivation due to adjacent lithography. (a) Rectangle formed by HDL following a serpentine path with 4 V, 4 nA, and 4 mC/cm line dose. (b) Same rectangle after HDL of nearby areas using same HDL conditions. Confirmed repassivation sites are circled.

III. DISCUSSION

Based on the results in Figs. 1 and 2, there is good evidence that the spurious DB formation is a result of H returning to the surface. The mechanisms that could result in spurious DBs due to the H include: the adsorption of the departing H onto a dimer resulting in three H atoms and one DB, and the extraction of an H atom from a dimer to form a liberated H_2 molecule leaving the dimer with a single H and a single DB. Typical monohydride UHV Si(100)-H sample preparation involves exposing a heated, unpassivated Si(100) sample to a source of atomic hydrogen,[16] usually involving a cracking filament in an atmosphere of H_2, while at room temperature, even more H is put onto the surface, resulting in significant dihydride formation.[17] However, the barrier for H extraction by physisorbed H is very low, suggesting a preference for H extraction instead of additional H chemisorption. This ambiguity is addressed below.

Detailed analysis of the surface as in Fig. 3 may provide clues to the DB production mechanism. For an unreconstructed Si(100), each surface Si atom contains two unbound electrons with pairs of atoms bonding together to dimerize in the absence of any passivating species. In the presence of H atoms, however, each Si dimer can nominally accommodate up to four hydrogen atoms, with cases for one to four atoms shown schematically in Fig. 3(a). Note that for an odd number of H atoms bound to a dimer, a DB is produced. Figure 3(b) shows a region of the Si(100)-H (2×1) surface with a vacancy defect as well as a dihydride defect. The dihydride defect consists of two H atoms bonded to each Si

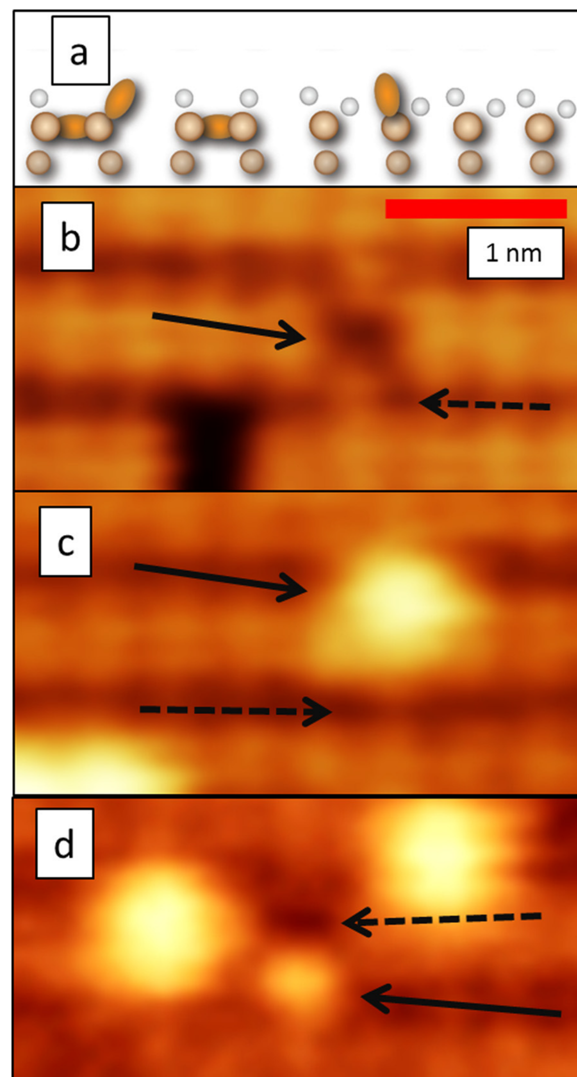

FIG. 3. (Color online) Images of dimers with various reconstructions. a: Side view schematic representations of the potential configurations of the Si dimer with one to four H atoms bonded to the topmost Si atoms, from left to right, respectively. H atoms are the small unfilled circles, with dangling bonds as well as the Si-Si dimer bonds indicated by the ellipses. (b) Si(100)-H surface with predominantly monohydride dimers. A dihydride dimer is pointed out with the solid arrow. Notice the raised trench between dimer rows at the dihydride dimer (dotted line). (c) Area of surface after spurious DB formation. The solid arrow shows the DB, and the dotted arrow indicates a nonraised dimer row trough next to the dangling bond. (d) Area with an additional type of dangling bond. The solid line indicates a protrusion, and the dotted line is the trough in the center of the dimer row with a raised area above the trough.

atom of the dimer. The dihydride has a node along the center of the dimer row and a raised trough between dimer rows. Figure 3(c) shows a region of the passivated surface with a single DB on a dimer. This DB was produced as a spurious DB but is topographically indistinguishable from a DB formed during sample preparation, with an identical height and no raised area in the trough at the bottom of the dimer row, suggesting it is indeed a single DB next to a monohydride. Figure 3(d) shows another feature formed during HDL that shares characteristics of a pair of dihydride atoms on a dimer row. This feature has a protrusion on one side of the dimer row, although this is smaller than the

single DB. It also has a node in the center of the dimer row with a raised area in the upper trough, suggesting that this is a single DB on an unsaturated dihydride dimer. A vast majority of the spurious DBs formed share the single DB conformation shown in Fig. 3(c), suggesting that product of the interaction of the liberated H with the surface is H_2 and a spurious DB.

It has been shown that exposing a deuterium passivated surface to atomic hydrogen does result in exchange of surface passivants at 273 K,[18] but with a yield of approximately 3%. In the case here, the observed probability of spurious DB production P_{obs} 5 $P_{phys}P_{DB}$, where P_{phys} is the probability of a liberated H physisorbing to the surface, and P_{DB} is the probability of a physisorbed hydrogen producing a spurious DB. The results presented in Table I show that the total P_{obs} (i.e., total #/pattern size) is approximately 15% for the 80 DB patterns and approximately 10% for the 200 DB patterns. However, this number does not account for P_{phys}, which can not exceed 1. Based on this, the observed probability P_{obs} of 10% indicates a lower limit to the reaction probability P_{DB}. These results do conflict with results expected from room temperature sample preparation using atomic hydrogen, suggesting the possibility that the reactivity of either the surface under the STM tip or the liberated hydrogen atoms may be different than during a room temperature sample preparation.[19]

The advantage of low voltage HDL is that it can produce very precise patterns, so the intrinsic formation of spurious DB defects can prove to be particularly insidious for applications where isolated DBs act as sites for surface functionalization. Some metals such as gallium[20] or organic molecules such as styrene[21] have shown an affinity for single DB deposition. Fortunately, for applications such as phosphorus incorporation,[3] patterned atomic layer deposition,[22] or even molecular deposition of disilane for patterned epitaxy,[2,23,24] multiple DBs are required to open up energetically favorable pathways for deposition. Also, since tip dependence [Fig. 2(d)] has been observed for the spurious DB production effect, it remains possible that careful tip engineering may dramatically reduce or control this effect, with a very low spurious DB production rates achieved,[11] and even selective passivation of the Si surface by tips saturated with hydrogen.[25,26]

IV. SUMMARY AND CONCLUSIONS

With the promise of atomically precise fabrication using HDL as an initial patterning step for surface functionalization, understanding all of the possible error mechanisms will be essential. This manuscript demonstrates that for low V HDL, the liberated hydrogen atoms play a role in production of dangling bonds up to 10 nm outside the primary patterning area. Besides spurious DB production, the liberated hydrogen has also been observed to repassivate previously passivated areas. While the mechanism of spurious DB production remains unknown, tip dependence has been observed, suggesting a tip mediated mechanism beyond simple electrical excitation.

ACKNOWLEDGMENTS

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