# Atomic precision patterning on Si: An opportunity for a digitized process

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**Abstract:**

H depassivation lithography is a process by which a monolayer of H absorbed on a Si(100) 2x1 surface may be patterned by the removal of H atoms using a scanning tunneling microscope. This process can achieve atomic resolution where individual atoms are targeted and removed. This paper suggests that such a patterning process can be carried out as a digital process, where the pixels of the pattern are the individual H atoms. The goal is digital fabrication rather than digital information processing. The margins for the read and write operators appear to be sufficient for a digital process, and the tolerance for physical addressing of the atoms is technologically feasible. A digital fabrication process would enjoy some of the same advantages of digital computation; namely high reliability, error checking and correction, and the creation of complex systems.

## 1. Introduction

The process of removing H atoms from the Si surface with a Scanning Tunneling Microscope (STM) is a well established experimental process [1]. There is a current effort to use H depassivation lithography to develop a patterned Si atomic layer epitaxial process to create three dimensional atomically precise Si structures [2]. It is tempting to consider the H depassivation patterning process as e-beam lithography with a self developing resist. However, the well ordered Si(100) 2x1 surface and the discrete nature of the monolayer H resist provides the opportunity to treat this patterning process as a digital fabrication process and capture many of the digitized advantages of digital computation, communication, and information storage.

We are proposing a digitized patterning process, and while we will use terminology that is common to digital memory, we do not propose information storage. Rather we claim that there are significant advantages to approaching physical patterning – that has always been treated as an analog process – as one which can be digitized. Other researchers have recognized the value of quantized lithography [3,4]. We assert this can be accomplished at the atomic scale. The Si(100) 2x1 reconstructed surface is very regular and individual surface atoms can be considered pixels. Each pixel (surface Si atom) either has an H attached or not, so its state is inherently binary. A pixel is patterned if the

H atom is removed. If the addressing, reading, and writing of each pixel can be accomplished with sufficient margins for high reliability, then we can realize the large advantages of a digital process, which include: reliable operation with well established tolerances, error checking and correction, no error accumulation, and the capability to create complex systems. We note that this is not atomic manipulation with an STM where two dimensional atomic or molecular structures can be created on a surface from species that are randomly deposited, but rather a lithographic process that should be able to achieve atomic resolution with high reliability.

## 2. Si (100) 2x1 Surface

The unreconstructed Si(100) surface is characterized by a regular grid of Si atoms spaced nominally 0.387nm apart, but this requires that each Si atom has two unsatisfied covalent bonds (referred to as dangling bonds). Typically, this surface reconstructs into dimer rows where each atom in a dimer shares a covalent bond, leaving one dangling bond per Si atom. This very reactive surface can be rendered relatively inert, or passivated, by reacting an H atom with the dangling bond, which leaves each Si atom with all four of its covalent bonds satisfied. The dimers are spaced by 0.387nm along the row and the dimer rows are on a 0.774nm pitch. The direction of the dimer rows changes by 90 degrees with each monolayer atomic step. On an atomically flat terrace all of the surface atoms are well arrayed in these dimer rows. In what follows we will assume that we have a perfectly formed Si 2x1 completely passivated surface.

H depassivation lithography is electron stimulated desorption carried out by an STM [1]. At relatively low biases (2-4 V), the desorption process depends on a multi-electron vibrational excitation mechanism which can allow depassivation lithography to be performed down to the single atom scale. An atomically precise pattern of 4x11 H atoms has been written with H depassivation lithography [5]. A property of the low bias writing technique is that the writing, or desorption, process is signaled by a significant increase in the tunneling current due to an increase in the tunneling probability into the high energy dangling bond upon removal of the H atom. This process of "feedback controlled lithography" can be used as an endpoint detection for the writing process [6] thereby making it a high reliability process.

## 3. Fabrication Operations

On the perfectly formed Si(100) 2x1 surface described above, we identify individual surface atoms by their position in the lattice using the indices (i,j) to define pixel $P_{i,j}$. Furthermore, we identify whether or not the state $|n\rangle$ of the surface at $P_{i,j}$ is passivated or unpassivated, which we will here define as states $|0\rangle$ or $|1\rangle$, respectively. Imaging and lithography likewise act as operators on these states. Imaging a specific $P_{i,j}$ will be defined as a READ operation and is represented by the product of operator and state $\hat{R}_{i,j}|n\rangle$. Similarly, lithography will be defined as a WRITE operation and is represented

by $\hat{W}_{i,j}|n\rangle$. Other operators may be used in the future, such WRITE_ZERO ($\hat{W}_{i,j}^{-1}$). We summarize these operations in Table 1.

Table 1: Fabrication operations

| State\Operator | $\hat{R}_{i,j}$ | $\hat{W}_{i,j}$ | $\hat{W}_{i,j}^{-1}$ |
|---|---|---|---|
| $\|0_{i,j}\rangle$ | $\|0\rangle$ | $\|1\rangle$ | $\|0\rangle$ |
| $\|1_{i,j}\rangle$ | $\|1\rangle$ | $\|1\rangle$ | $\|0\rangle$ |

The rest of this manuscript will explore the validity of some of the assumptions behind generating Table 1. One question that needs to be answered is what are the various error rates for the operators. For example, it has been shown that the $\hat{W}_{i,j}$ operation can be done with atomic precision, but care must be taken to avoid the operation $\hat{W}_{i,j}|0_{k,l}\rangle = |1\rangle$ which is an inadvertent WRITE on the unaddressed pixel $P_{k,l}$.

**4. The READ operator**

The STM typically images by raster scanning the tip across the surface while using a feedback loop to adjust the height of the tip to maintain a constant current. Typical imaging conditions include sample biases in the range of +2 to -2 V and tunneling currents on the order of 50pA. When scanning the surface of a single material, this process typically reveals the topography of the surface with atomic resolution. However, when the surface has spatial variation in the electron tunneling probability then the "topographical" image is convolved with the tunneling probability. Such is the case of a Si (100) 2x1 surface with partial H passivation. A passivated Si atom has a lower tunneling probability than a Si atom with a dangling bond since the dangling bond more readily accepts the electron. The result is that a missing H atom looks like a raised area approximately 0.15nm tall, which is well within the typical STM height resolution of a few pm. However, the usual mode of STM imaging is inefficient and we propose instead that $\hat{R}_{i,j}|n_{i,j}\rangle$ be the physical addressing for that pixel and that we "read" the state by measuring the height of the tip at a particular set point current (or by measuring the current at a particular set point height). By choosing the $\hat{R}_{i,j}|n_{i,j}\rangle$ conditions appropriately, the possibility of an inadvertent WRITE, $\hat{R}_{i,j}|0_{i,j}\rangle = |1\rangle$, can be very low. At low biases, the $\hat{W}_{i,j}|n_{i,j}\rangle$ yield exponentially depends on current [1]. Extrapolating from data of Shen [7], for a sample bias of 2V and a current of 50pA the desorption yield is $2\times10^{-15}$ atoms/electron. For a conservative $\hat{R}_{i,j}|n_{i,j}\rangle$ time of 1ms at 50pA the

$\hat{R}_{i,j}\left|0_{i,j}\right\rangle = \left|1\right\rangle$ probability would be less than 1x10$^{-9}$. If the $\hat{R}_{i,j}\left|n_{i,j}\right\rangle$ were carried out with a negative sample bias the $\hat{R}_{i,j}\left|0_{i,j}\right\rangle = \left|1\right\rangle$ rate would be further reduced [8]. In experiments carried out in our Ultra High Vacuum (UHV) STM at base pressures of ~2x10$^{-10}$ Torr, extended scanning over a small area at a -2.25V bias and 50pA current, changes in the imaging that could be associated with $\hat{R}_{i,j}\left|0_{i,j}\right\rangle = \left|1\right\rangle$ (but could also include other effects) occurred at a rate of 8x10$^{-4}$ per second which would correspond to a probability of 8x10$^{-7}$ for $\hat{R}_{i,j}\left|0_{i,j}\right\rangle = \left|1\right\rangle$ with a 1ms read time. This should be considered an upper bound on the $\hat{R}_{i,j}\left|0_{i,j}\right\rangle = \left|1\right\rangle$ probability.

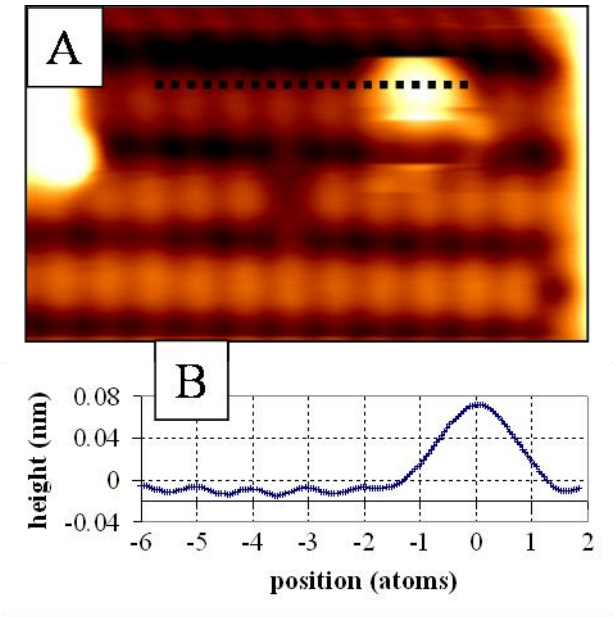


Figure 1. A 4.6x2.9nm STM image showing a single dangling bond along a dimer row. The STM image is shown in part A, with a profile along the dotted line shown in Part B. In the profile, the horizontal axis has been scaled to pixel index *i* relative to the dangling bond at index *i*=0.

Given the physics of the STM, there will be a proximity effect in $\hat{R}_{i,j}\left|n_{i,j}\right\rangle$ due to a dangling bond at a neighboring $P_{i,j}$. Figure 1 shows an STM topographical profile of 8 Si atoms where one of the atoms is in state |1>. While the topographical signal of the two pixels on either side to the written atom are raised, it would still be possible to distinguish a |1> from |0> with a simple threshold of 0.04nm.

**5. The WRITE Operator**

As one of the three crucial components of digital construction is a robust $\hat{W}_{i,j}\left|n_{i,j}\right\rangle$, in Figure 2 we demonstrate a step towards an atomically precise $\hat{W}_{i,j}\left|n_{i,j}\right\rangle$ on H-Si(100).

While numerous groups have demonstrated atomically precise depassivation of hydrogen from silicon [1,6,9,10] this document goes one step further and examines the effect of $\hat{W}_{i,j}\left|n_{i,j}\right\rangle$ under differing starting conditions. First, we addressed the surface by imaging a very small area as shown in fig. 2(A)—this represents an area that is almost entirely |0> except for intrinsic surface defects. Next, we performed $\hat{W}_{i,j}\left|n_{i,j}\right\rangle$ along a line on the center dimer row by moving our tip at 10nm/s using 4.75V and 2nA. Figure 2(B) shows a nearly solid |1> pattern along the target dimer row with two easy to see defects: in the left surface vacancy $\hat{W}_{i,j}\left|0_{i,j}\right\rangle = \left|0\right\rangle$, and along an adjacent dimer row $\hat{W}_{i,j}\left|0_{k,l}\right\rangle = \left|1\right\rangle$. Next, we performed $\hat{W}_{i,j}\left|n_{i,j}\right\rangle$ along the dimer row below the original set of |1> states using the same conditions as in fig. 2(B) with results shown in fig. 2(C). This second $\hat{W}_{i,j}\left|n_{i,j}\right\rangle$ showed three types of errors: a few cases where $\hat{W}_{i,j}\left|0_{i,j}\right\rangle = \left|0\right\rangle$, an instance of $\hat{W}_{i,j}\left|0_{k,l}\right\rangle = \left|1\right\rangle$, and re-addressing an already existing |1>. While improvements in $\hat{W}_{i,j}\left|n_{i,j}\right\rangle$ need to be made, it is indeed possible to perform $\hat{W}_{i,j}\left|n_{i,j}\right\rangle$ in non-homogenous environments without any sophisticated procedures such as feedback controlled lithography [6]. We acknowledge this will be a slow process compared to more conventional patterning techniques. For instance the dose required for the patterning process is $2.6 \times 10^4$ C/cm$^2$ which is approximately 7 orders of magnitude higher than for high resolution e-beam lithography[11]. However, e-beam lithography has not demonstrated atomic resolution and could not read without writing.

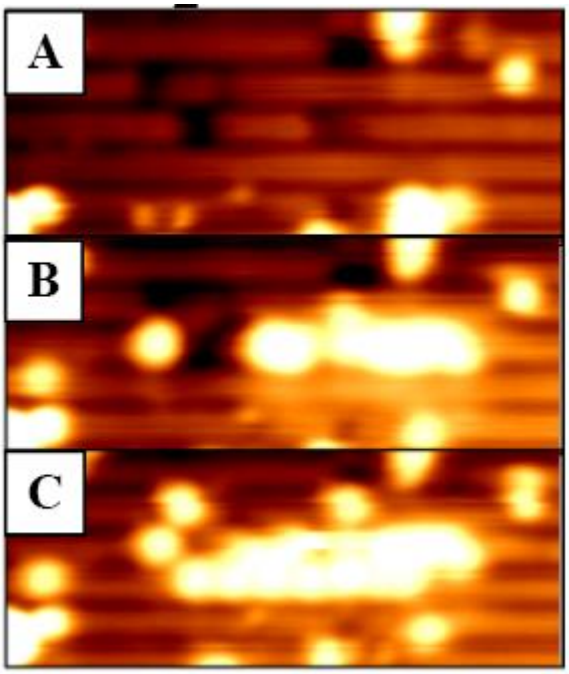

Figure 2 STM images of a 4.3x11nm H-passivated Si(100) surface. Part A is prior to patterning; part B is after performing a $\hat{W}_{i,j}\left|n_{i,j}\right\rangle$ along the third dimer row; and part C is after performing a $\hat{W}_{i,j}\left|n_{i,j}\right\rangle$ along the fourth dimer row.

**6. Addressing Pixels**

As mentioned above, the Si atoms on an atomically flat (100) terrace are arrayed in a regular pattern, and we assume a perfect initial surface. While in practice, such perfect surfaces are difficult to prepare over large areas, defects are easily detected, avoided, and in some cases may be ignored or repaired. Since STMs have the spatial resolution to observe the individual atoms on this surface, it seems likely that individual atoms could be reliably addressed. However, a standard STM image consists of significant oversampling, so more efficient addressing schemes are possible. In either case, sample drift and other practical issues must be overcome.

In order to reliably address each pixel in a given fabrication area to perform $\hat{R}_{i,j}\left|n_{i,j}\right\rangle$ or $\hat{W}_{i,j}\left|n_{i,j}\right\rangle$, we must position the tip to a tolerance on the order of 0.1nm. The two atoms in a dimer are separated by 0.26nm, so an upper bound of the required tolerance is 0.13nm. Writing experiments suggest that a suitably sharp tip simply has to be closer to the target atom than to any other to depassivate that atom, though there is some evidence that a tip directly over a dimer may desorb both H atoms [12]. A reliable $\hat{R}_{i,j}\left|n_{i,j}\right\rangle$ by sampling once within the 0.1nm spatial tolerance may or may not be possible. A tip without high enough spatial resolution may require a more sophisticated measurement, such as sampling a number of points in the vicinity in order to read an atom with a neighboring dangling bond. A successful approach – whether single measurement or more sophisticated sampling – will need to work within the spatial tolerance of the addressing system and the tolerance of the tip spatial resolution. There are interferometers on the market with better than 40pm resolution [13] which suggests that spatial addressing to within 0.1nm is possible without relying on STM imaging.

Whatever process is used to address a particular pixel must contend with some sample drift. We have developed an algorithm that measures and corrects for drift in our UHV STM [14]. We took drift measurements once every 5.9 minutes and after an initial period of several minutes of relative instability, over the next 7 hours there was over 150nm of sample drift but the drift correction algorithm kept the average positional error to 0.49nm and the maximum error was 1.36nm. This suggests that drift corrections every 25 seconds would maintain spatial drift errors of less than 0.1nm in our system. We note that this is only one component of the spatial error and more frequent corrections would likely be required. However, using the Si lattice as a fiducial grid would mean that the overhead for drift measurement could be very low because the grid can be sampled as the tip moves [15]. This would amount to "align on the fly". Further, we believe that the drift and drift changes can be reduced. Our measurements include some tip variations which

introduce apparent sample drift and could be avoided with more robust tips. Also, improved control of the local environment would reduce the drift. We can already identify the positions of a small field of specific atomic sites and reliably address them for a period of time long enough to do simple patterning. Additional work will be required to expand the number of pixels and time between corrections.

## 7. Challenges

There are still a number of challenges to developing a reliable digital fabrication process. In our view the three most significant are: improving the tips, reducing surface defects, and finding a process for repairing clear defects. Both $\hat{R}_{i,j}\left|n_{i,j}\right\rangle$ and $\hat{W}_{i,j}\left|n_{i,j}\right\rangle$ are strongly affected by the imaging resolution of the notoriously variable STM. Improvements in the control of tip performance and robustness are essential. Using current sample preparation techniques, small areas of "perfect" Si surfaces are already possible, but larger areas need to be reliably produced. It should be noted that some defects can be tolerated or repaired. One operator that we do not have a process for at present is $\hat{W}_{i,j}^{-1}$ (replace a missing H atom).

## 8. Conclusions

We have proposed a digital fabrication process of H depassivation lithography on a Si (100) 2x1 surface. The tolerances for read, write, and addressing suggest that a digital process is possible, but that challenges remain.

## 9. Acknowledgements

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## References

1. Michael A. Walsh and Mark C. Hersam; Annu. Rev. Phys. Chem.. 60:193–216 (2009).
2. http://www.darpa.mil/MTO/programs/tbn/pdf/Zyvex_TBN.pdf
3. Nadim I. Maluf, and R. Fabian Pease, Journal of Vacuum Science and Technology **B9** (1991) 2986-2991 and
4. Wen-Di Li, Xiaogan Liang and Stephen Y. Chou, "Negative Tone Quantum Lithography at 200-nm Pitch Nanoimprinted Blanks", Presented at the International Conference for Electron, Ion, and Photon Beam Technology and Nanofabrication, May 26-29, 2009 Marco Island Florida.
5. Private communication with Joseph Lyding, University of Illinois
6. M C Hersam, N P Guisinger and J W Lyding; Nanotechnology **11** 70–76 (2000).

7. Shen TC, Wang C, Abeln GC, Tucker JR, Lyding JW, et al.; *Science* 268:1590–92 (1995)
8. K. Stokbro, C. Thirstrup, M. Sakurai, U. Quaade, Ben Yu-Kuang Hu, F. Perez-Murano, and F. Grey; *Phys. Rev. Lett.* 80:2618–21 (1998).
9. X. Tong, R.A. Wolkow; Surface Science 600 L199–L203 (2006).
10. Simmons MY, Schofield SR, O'Brien JL, Curson NJ, Oberbeck L, et al.; *Surf. Sci.* 532:1209–18 (2003)
11. Sung-Wook Nam, M. J. Rooks, Joel K.W. Yang, Karl K. Berggren, Hyun-Mi Kim, and Ki-Bum Kim, "Contrast Enhancement Behavior of Hydrogen Silsesquioxane (HSQ) in a Salty Developer" Presented at the International Conference for Electron, Ion, and Photon Beam Technology and Nanofabrication, May 26-29, 2009 Marco Island Florida.
12. Ph. Avouris et al; Surface Science 363 (1996) 368-377
13. For instance theRenishawRLD10-X3-DI differential interferometer, has reported resolutions to 38.6 pm. http://www.renishaw.com/en/6492.aspx#tocTarget0
14. J.N. Randall, J.W. Lyding, S. Schmucker, J.R. Von Ehr, J. Ballard, R.Saini, H. Xu, Y. Ding; Accepted for publication JVSTB
15. Henry I. Smith, Scott D. Hector, M.L. Schattenburg, and Erik H. Anderson; Journal of Vacuum Science and Technology **B9** (1991) 2992-2995