Patterned Atomic Layer Deposition on Scanning Tunneling Microscope constructed templates

Joshua Ballard**, Stephen McDonnell*, Don Dick*, James Owen**, Greg Mordi*, Angelica Azcatl*, Philip Campbell*, Yves Chabal*, John Randall**, Robert Wallace**

*University of Texas at Dallas, Richardson, TX, USA
**Zyvex Labs, Richardson, TX, USA
jballard@zyvexlabs.com

ABSTRACT

Structures created through Atomic Layer Deposition (ALD) of titania (TiO_2) on top of Scanning Tunneling Microscope (STM) based hydrogen depassivated patterns on Si(100) are demonstrated. The UHV prepared samples retain their patterns after exposure to atmosphere, with high selectivity shown between patterned areas and background. Atomic Force Microscopy (AFM) measurements indicate correlation between hydrogen depassivation saturation in the STM patterned areas and the resulting height of the deposited TiO_2. Additionally, it is shown that for the narrowest linewidths, there is a correlation between linewidth and height of the TiO_2 structure. After deconvolution of tip shape with the observed AFM linewidths, patterned ALD lines with heights of 2.5 nm and widths of less than 6 nm are observed.

Keywords: Scanning Tunneling Microscopy, Atomic Layer Deposition, Nanostructure Fabrication, Patterned Growth

1 INTRODUCTION

Hydrogen-depassivation lithography using a Scanning Tunneling Microscope (STM) has been used to selectively functionalize surfaces with the possibility of atomically perfect patterning on size scales down to 1.5Å [1]. Using this technique, researchers have constructed both 2-D and 3-D structures of various materials [2] [3], on several substrates, but primarily on Si(100)-H. While STM depassivation lithography is an inherently slow process due to its serial nature, structure fabrication processes that involve a single STM patterning step may be advantageous over processes requiring multiple patterning steps. To this end, this research shows a process combining STM lithography with the well controlled technique of Atomic Layer Deposition (ALD), indicating a new process for using single-pass STM patterning for fabrication of 3-D structures with sub-nanometer dimensional control.

In order to perform patterned ALD, growth should selectively occur in the areas patterned using STM lithography without any growth on the passivated background. Several species have previously been shown to selectively react on the depassivated patterns [4], including at least one chemistry commonly used in ALD—$TiCl_4 + H_2O$, albeit in monolayer quantities [5]. In order to find a selective ALD chemistry, growth was performed on unpatterned samples that were chemically terminated with SiOx or Si-H. The deposited surface thicknesses were inferred by measuring the ratio of the metal to silicon features using XPS. The TiO_2 process using $TiCl_4$ and H_2O, shows excellent selectivity between the oxidized and passivated surfaces, as demonstrated in Ref [6]. From this basis, this manuscript describes the process of performing patterned ALD, shows the dependence of depassivation saturation and linewidth on deposition quality, and describes process and analysis limitations.

2 PROCESS AND TOOLS

Si(100)-H samples are prepared and patterned in UHV, transported for deposition in an *ex situ* ALD chamber, then transferred to an *ex situ* AFM. The first step of sample preparation is to mark the surface with optically accessible fiducial structures, which achieves a dual purpose: to assist in locating STM patterns after removal from the STM and to aid in the preparation of large (>10 μm^2) atomically flat Si(100) terraces. Samples are cleaned in acetone, isopropanol, methanol, and deionized water, then inserted into the UHV preparation chamber (base P ~$1x10^{-9}$ Torr) where they are degassed for 16 hours at 650 ^oC, flash cleaned for four 20 s cycles at 1245 ^oC, then annealed for up to 4 hours at 1000 ^oC to prepare large terraces. Finally the samples are passivated for 12 minutes in an atmosphere of $1.5x10^{-6}$ Torr of H_2 with a cracking filament located ~6 cm from the sample heated to 1450 ^oC. After preparation, the samples are moved to the UHV-STM chamber (base P ~$8x10^{-10}$ Torr) where they are inserted into the Lyding-style STM [5]. A long working distance microscope observes the tip position on the sample with a positional uncertainty of ~8 μm before transfer to ALD and AFM.

The STM was perfomed with electrochemically etched and sputter sharpened tungsten tips [6]. Imaging is typically performed with a sample bias of -2.25 V and tunnel current of 0.15 pA. Lithography was performed with a sample bias of 8 V, current of 0.5 nA, and line dosage of 0.1 mC/cm (corresponding to a tip speed of 50 nm/s) unless otherwise noted. At least five specific depassivation patterns are written into the surface, as shown in fig. (1). In order to facilitate feature identification with AFM, three 800 nm ×

800 nm serpentine patterns are written with a 30 nm line pitch, with each pattern spaced by approximately 1 μm. Spaced 1 μm laterally from these serpentine patterns can be found finer experimental patterns where either the linewidth or line dosage was varied. After at least five patterns are written in one area, the tip is translated across the sample typically by tens of microns, and the patterns are repeated.

After patterning, the sample is removed from the UHV system through a load lock that is vented with dry nitrogen using all stainless steel tubing. After a few minutes of atmospheric exposure, the samples are mounted into a sample storage/transport unit and stored for up to a few hours under approximately 1.1 bar of argon. The samples are then removed from the transport unit and inserted into the ALD chamber (Cambridge Nanotech Inc., Savannah 100). After a 60 minute settling of the temperature to 100°C, ALD is performed with alternating saturating cycles of $TiCl_4$ and H_2O. After the prescribed number of ALD cycles, the samples are removed from the ALD reactor and either stored in the transporter unit or carried to the AFM for immediate analysis. AFM is performed (Digital Instruments AFM Nanoscope Dimension 3100) with either new bare (Bruker, Inc) or HfB_2 coated silicon tips (Tiptek, Inc.) to assure both sharpness and long term robustness.

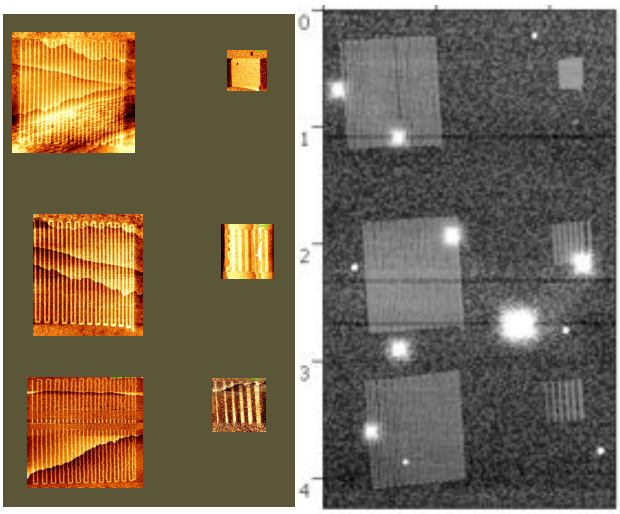

Figure 1: STM and AFM pattern overview. Three 800 nm x 800 nm serpentine patterns are used to ease locating the smaller patterns after ALD. The smaller patterns are used to study flatness, depassivation saturation, and linewidth, from top to bottom, respectively.

3 RESULTS

While the selectivity of TiO_2 deposition between hydrogen terminated Si and oxidized or clean silicon surfaces has been shown, the dependence of the degree of passivation has not been shown. In order to quantify this, one of the control patterns includes a gradient of saturation levels, as shown in fig. (2a). The STM patterns were written in a serpentine path with a 5 nm pitch for a total of six lines. With a nominal Gaussian FWHM of 5 nm, this assures a relatively uniform saturation level across each line. From left to right, the lines are written with a line dose of 10 μC/cm to 70μC/cm, (500 nm/s to 71 nm/s). This yields a depassivation saturation of approximately 0.35 to 0.8 (i.e. 35% to 80% depassivated).

Figure (2b), which shows TiO_2 growth after 80 cycles of ALD, has a clear selectivity between the patterned areas and the unpatterned areas with a weak dependence on saturation level. A section averaging 128 data points is taken across this image in order to determine the height as a function of depassivation, as shown in fig. (2c). The cross section is leveled using the minimum measured heights on either side of the pattern in order to limit the effect of background growth on the measurements. Figure (2 c&d) show that there is a nonlinear relationship between depassivation saturation and the observed line height, suggesting that growth along the patterned lines can occur with less than complete hydrogen depassivation.

Since the true power of this technique of combining STM with ALD arises from the superb patterning precision of STM based hydrogen depassivation lithography, the effectiveness of ALD growth as a function of pattern

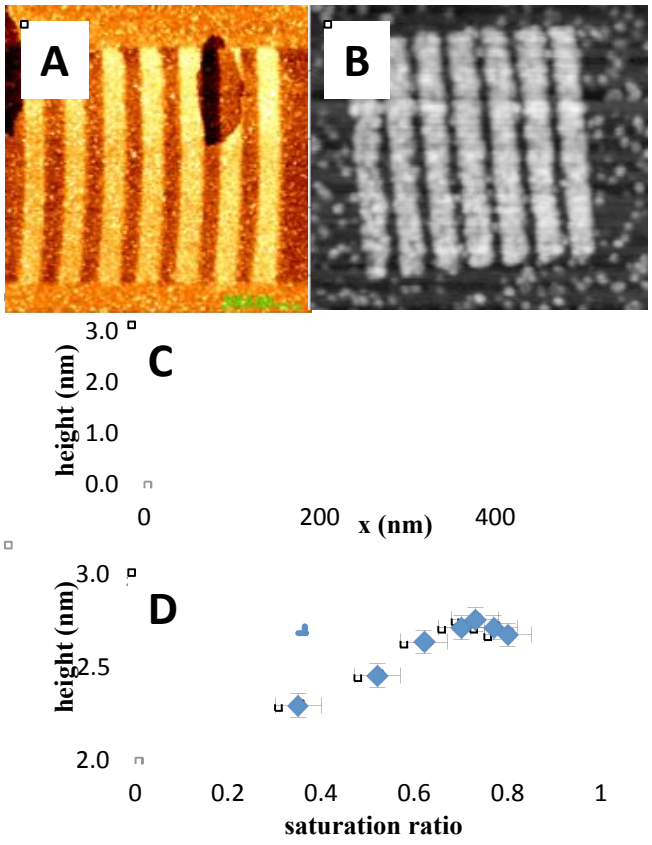

Figure 2: Hydrogen depassivation saturation dependence of ALD growth. A pattern set with 300 nm long rectangles was written with doses ranging from 0.01mC/cm to 0.07mC/cm. Writing conditions were 8 V and 0.5nA. Part A is an STM image of the pattern after lithography, and part B is an AFM image of the pattern after 80 cycles of ALD. Parts C and D summarize cross section data from part B.

linewidth was also studied. The results are summarized in fig. (3). The STM linewidths [fig. (3a)] vary from 12 nm to 32 nm FWHM with completely saturated linewidths approximately 6 nm less than that. After ALD, there appears to be a somewhat shorter structure in the narrowest lines, as shown in fig. (3b-d). As a function of linewidth, there seems to be a threshold above which the ALD depth is independent of pattern width, but below that width, there seems to be a pattern width dependence.

4 DISCUSSION

The success of the selectivity depends not only on the ability to perform ALD within the STM patterned areas, but also it depends on avoiding deposition on the hydrogen passivated background. To that end, TiO_2 ALD was performed on a variety of unpatterned control samples of Si(100) that underwent a variety of processes, including flash cleaning in UHV followed by atmospheric exposure, chemical oxidation, chemical hydrogen passivation, and hydrogen passivation in UHV followed by exposure to atmosphere.

After 46 cycles of ALD, the TiO_2 thicknesses were measured using XPS [6], and it was confirmed that there is a selectivity greater than 100 for the oxidized samples relative to the chemically passivated samples, with deposition depths of 15.6Å and 0.11Å, respectively, where the 0.11Å corresponds to an effective coverage of 4% of a monolayer. The UHV prepared hydrogen-passivated samples showed a slightly higher deposition depth with typically 10% of a monolayer.

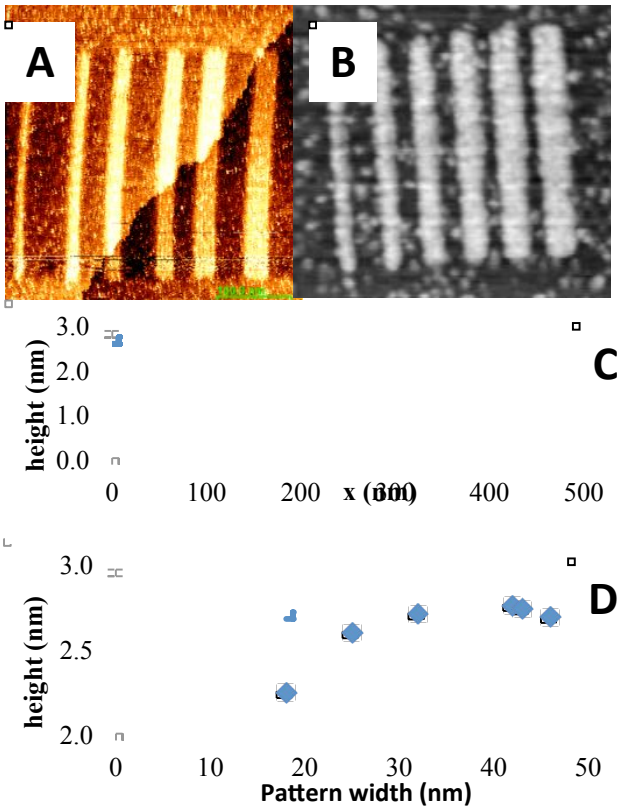

Figure 3: Linewidth dependence of pattern height. Parts A & B show STM and AFM images of a set of lines with increasing linewidth. Parts C & D summarize cross section data from part B. The pattern with of part D is based on the FWHM of each line in part C.

Within the patterned areas where complete hydrogen passivation has occurred, uniform deposition is observed with a roughness nearly equal to the roughness observed on an unpatterned chemically oxidized sample. Additionally, the layer tihckness, as measured with AFM, agrees within 10% with the layer thickness for unpatterned samples as measured with XPS [6]. This suggests that the spontaneous oxidation of the surface upon exposure to atmosphere is adequate for effective TiO_2 ALD. However, the ALD process begins with a dose of H_2O which should adequately seed the surface for ALD patterning. Still, it is confirmed that relatively uncontrolled exposure to multiple laboratories' atmospheres does not limit the growth within the patterned areas.

The structure of the ALD layer within the patterns is still unknown, but some aspects of the growth dynamics can be ascertained by the AFM analysis. For the STM patterns, there is a rolloff of hydrogen depassivation saturation as the distance away from the center of the line or pattern increases. After ALD, this rolloff manifests itself as a line-edge roughness with identifiable grain boundaries. Whether or not this can be attributed to different phases of TiO_2, simple roughness, or phase or orientation boundaries between similar crystal structures of TiO_2, cannot be determined from the ALD results. However, previous results on TiO_2 ALD on large samples grown at 120 ^oC have shown that primarily amorphous structures dominate [7].

An apparent disagreement occurs when comparing the AFM analysis of the background of patterned samples and other unpatterned samples. XPS suggests a coverage of not much more than 25% of a monolayer of titanium in a worst case scenario, but the AFM shows a total volume of TiO_2 deposition on the background of several monolayers. This can be attributed to tip convolution effects. After ALD, XPS, and AFM, a sample was introduced into an UHV-STM with a 30 minute degassing anneal at ~300 ^oC; at this temperature, the modification of the TiO_2 on the surface should remain minimal, even though TiO_2 deposited at 300 ^oC deposits primarily in its anatase form [7]. Using the known sharp STM tip [6], the surface was imaged at a sample bias of -2.25 V and 100 pA. The STM analysis shows a much smaller island size, with a maximum of ~16% of the surface area covered with islands ranging in height from a single atom up to ~3 nm, in contrast to an apparent coverage of ~56% as observed by AFM. Given an approximate 1/3 contribution of Ti to the volume of TiO_2, and an expected tip radius of curvature of 2 nm (minimum), this indicates a total surface coverage of about 8% in close agreement with XPS data for a chemically passivated surface.

The tip convolution also causes an over-estimation of the linewidths of figs. (2 & 3). Based on fig. (4), the AFM tip broadens the TiO_2 island size by 10.0 nm relative to that

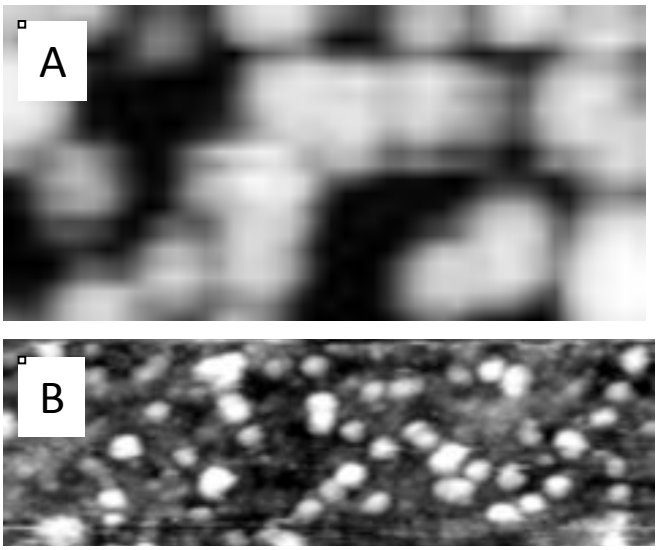

Figure 4: Comparison of AFM and STM analysis of samples after 80 cycles of ALD. Both images are 100 nm across. Part A shows a segment of an AFM image, and part B shows an STM of a similarly processed sample.

observed by STM. Thus, with a minimum STM tip radius of 2 nm, the AFM results over-estimate patterned linewidths by a minumum of 12 nm. This means that the minimum observed linewidth for lines produced using this method are on the order of 6 nm. This agrees well with the observation of a 5 nm saturated region of the narrowest line of the STM image of fig. (3a).

STM analysis of samples prior to exposure to atmosphere show a background dangling bond density on the order of 10^4-$10^5/\mu m^2$. Also, additional dangling bonds may be formed during the venting process [8]. Ab initio calculations suggest that a single dangling bond may be sufficient for seeding TiO_2 ALD, but perhaps two adjacent dangling bonds would better facilitate the formation of Si-O-H species on the surface. The occurrence of adjacent dangling bonds on the surface is much lower than for isolated dangling bonds, possibly explaining the large separation between observed islands on the surface. This may also play a role in explaining the nonlinear dependence of ALD on depassivation saturation.

Finally, the results shown in fig. (4) indicate that there is a significant tip convolution in the AFM results. Given this, there may be a significant overestimation of the volume extended by the adsorbed TiO_2. A comparison of the AFM and STM surface areas indicate that the AFM may overestimate the area by a factor of three or more for diffuse deposition patterns. Since the cross sections in figs. (2 & 3) are taken over a large portion of the line length, a tip convolution would overestimate the average height measurement. This may be due to an inconsistent island growth along the diffuse or narrow lines.

The pattern generation consists of several factors including template patterning, effective ALD on the templates, and resistance of the untemplated areas to ALD. In the context of this study, the precision of the patterning was kept less than atomically precise in order to facilitate throughput, so pattern widths were typically larger than 10 nm with depassivation saturation rolloffs over a spatial scale of approximately 3-5 nm on each side of a line. It has been shown that saturation rolloffs can be reduced to zero, i.e. to atomic precision [1]. This would certainly affect the quality of the ALD line edges, but it remains outside the scope of this study.

5 CONCLUSION

This study demonstrates patterned ALD growth of TiO_2 on patterned Si(100) where the patterns were formed by STM-based hydrogen-depassivation lithography. Very good selectivity between STM patterned and unpatterned areas was observed. AFM analysis of the ALD structures shows that there is a weak dependence on hydrogen-depassivation saturation, but there seems to be a fairly strong dependence on the lateral extent of the depassivation patterns. Good agreement between AFM data and XPS is observed on large, completely saturated patterns, and the XPS supports AFM data for background deposition.

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