Selective-Area Atomic Layer Deposition (SA-ALD) of Titanium Dioxide (TiO$_2$) using Poly(methyl methacrylate) (PMMA)

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Introduction

The Minnesota Nano Center's Keller Hall facility includes an atomic layer deposition (ALD) machine that is capable of depositing uniform alumina (Al$_2$O$_3$), hafnium oxide (HfO$_2$), silicon dioxide (SiO$_2$), zinc oxide (ZnO), and titanium dioxide (TiO$_2$). ALD works by building alternate layers on a film using two different precursor gases – one usually supplying the metallic atoms and water vapor (H$_2$O) usually supplying the oxygen atoms.

Under normal conditions, ALD is known to be extremely useful since the resulting film is very uniform, and its thickness is linearly related to the number of loops (number of alternating precursor gas cycles) set for a deposition. The uniformity results from the ability of the precursor gases to adsorb onto all available surfaces of a substrate (or a wafer) allowing the other precursor gas to build-off on top of the initial layer.

There has been recent research that examines TiO$_2$ film growth on patterned PMMA surfaces. Färm et al[1] noted that the growth of TiO$_2$ could be blocked on PMMA surfaces depending on the precursor gases. If the Ti source came from TiCl$_4$, TiO$_2$ was able to grow on the PMMA surface. However, if the Ti source were to be Ti[OCH(Me)$_2$]$_4$, no resulting TiO$_2$ film was observed.

Keller Hall's ALD machine utilizes tetrakis (dimethylamido) titanium (IV) (TDMAT) as the titanium source, and this reports investigates the resulting SA-ALD TiO$_2$ films grown on patterned PMMA surfaces.

This method of depositing ALD films is useful. Typically ALD films are used as high-k dielectrics (as is the case of HfO$_2$), transparent conductors (as is the case of doped ZnO), or as high index-of-refraction films (TiO$_2$). Thus, it is desirable to pattern the ALD films in order to localize their utility. Typically, this is done by depositing a uniform ALD film over the entire substrate, and then selectively etching the deposited film. However, etching usually needs to be done via wet etching (using buffered oxide etch, BOE) or relatively slow dry etching.

If the ALD film can be grown as a pre-patterned film using PMMA as a masking layer, the only additional processing step consists of lifting off the PMMA after the deposition.

Experimental (Materials & Methods)

Materials

The substrates used are either bare silicon (Si) or bare silicon with a thin (~950-1000Å) layer of thermal oxide (polymon) wafers. Polymon wafers are used to easily identify the thin (~200Å) TiO$_2$ films grown, since their contrast to the substrate is higher on the blue polymon wafers (white-to-blue as opposed to a dull brown-on-silver color).

PMMA films[2] came from a chlorobenzene-PMMA solution (MicroChem, 950 C9) where 950 refers to the 950 kDa molecular weight of the PMMA in solution, and C9 refers to a 9 weight percentage of PMMA. In

addition to 950 C9, a 1:1 volume-diluted solution was prepared using pure chlorobenzene to dilute the PMMA concentration weight to ~4.5% ("thin" 950 C9).

To pattern the PMMA films, either Shipley's Microposit S1813[3] or AZ's MiR 701[4] resist was used for contact-aligner (Karl-Suss MA6) and stepper (Canon i-line FPA) photolithography respectively.

Development of the exposed photoresist was done in Shipley's 351 developer (NaOH-based) for S1813, or in Microposit's MF CD-26 developer (TMAOH-based) for AZ MiR 701.

PMMA and PR removal was done by using either a series of solvent baths (acetone, methanol, isopropyl alcohol) or by O_2 ashing using the STS etcher. In some cases, ultrasonic agitation was used to enhance substrate cleaning when substrate with PMMA was soaked in acetone.

Film thickness characterization was done using a Gaertner ellipsometer, a Filmetrics spectral reflectance F50 machine, a Tencor P-16 profilometer, or a Digital Instruments Dimension 3000 atomic force microscope (AFM). Digital microscope images were obtained by using a Canon microscope in Bay 2, or the Nikon zoom microscope in Bay 1.

Methods

Starting from the substrate (bare Si or polymon) wafers, the PMMA solution (both regular & thinned) was spun-on using the headway spinner located in Bay 2. The max RPM was 3,000 RPM, and the speed was maintained for 30s.

Next, the substrate is soft-baked on a hot-plate at 160°C for 60s. This temperature is chosen in order to ensure that no solvent (chlorobenzene) will evaporate in the ALD chamber, where the deposition temperature is held at 150°C. The photoresist is now spun-on using the Canon 3,000 RPM recipe on the CEE-3 spinner in Bay 2. After the 30s spin, the wafer is soft-baked at 105°C if using S1813, or 90°C if using AZ MiR 701. Note that these temperatures lower than 150°C should not be a problem, since no photoresist should remain when putting the wafer into the ALD chamber.

If using the contact-aligner, the 4.5s soft-contact expose is done with the 3M test mask on the MA6, followed by a 30s develop in 351 Developer. The wafer is then DI-water rinsed and dried.

If using the stepper, a FEC (focus-exposure check) is performed with the focus ranging from -1.0 to +1.0μm and the exposure from 150 to 375 mJ/cm^2 using the super-illumination test reticle. Afterwards, a post-exposure bake at 115°C for 60s is done, and after being air-cooled, the wafer is developed for 30s in a fresh CD-26 crystallization dish bath. The wafer is then DI-water rinsed and dried.

At this point, the wafer is O_2 ashed in the STS etcher using the O2Clean recipe. The time varied depending on the sample, but the goal is to 1) eliminate the photoresist on top of the PMMA layer and 2) expose the substrate beneath the PMMA layer in preparation for ALD.
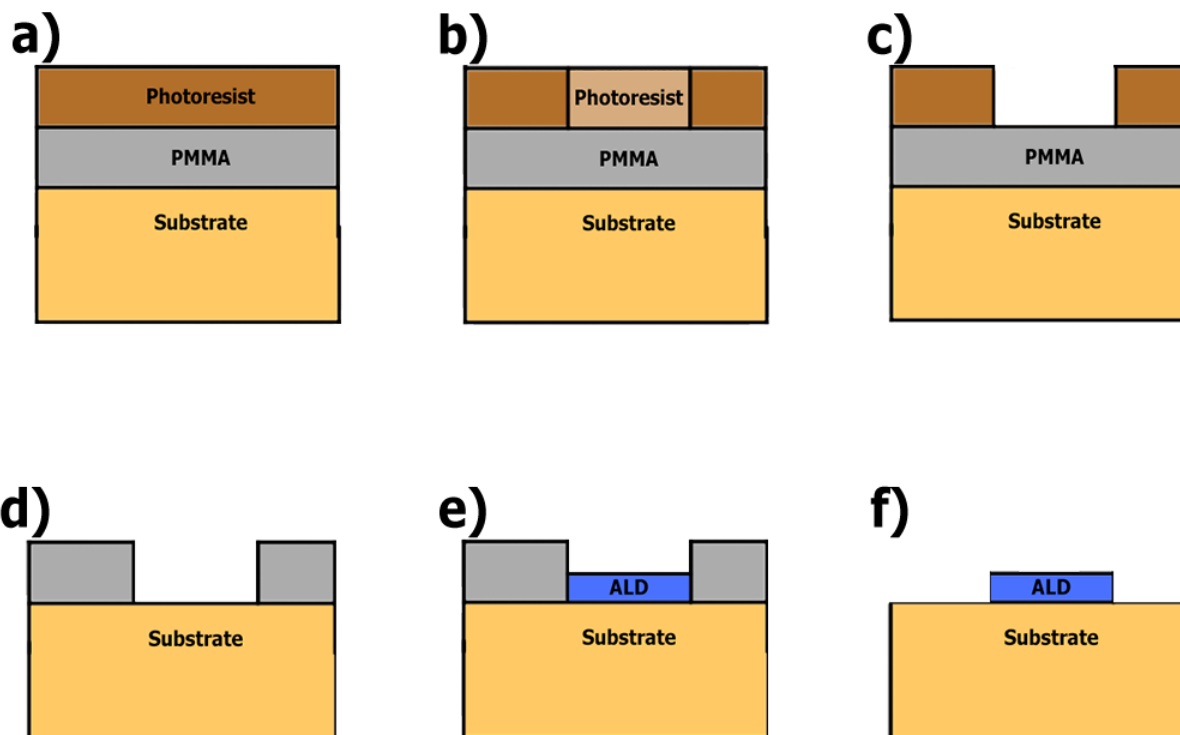
Figure 1. The steps for the SA-ALD process are shown. After PMMA and photoresist are spun on the substrate (a), the wafer is exposed and developed (b and c). An O_2 ash exposes the substrate and leaves behind a patterned PMMA layer (d) where the ALD film can be grown (e), and the PMMA removed (f).

The last step consists of removing the remaining PMMA layer. This was using one of two methods – ultrasonic agitation within an acetone bath, or a final O_2 clean step in the STS etcher. If done using ultrasonic agitation, the wafer or wafer pieces were put in a crystallization dish with acetone and placed in the ultrasonic bath in Bay 2. The power was set to a setting between 50 and 80 (out of 100), but some wafer pieces broke after being left at 80 for an hour. O_2 clean times ranged anywhere from 5 minutes to 30 minutes, depending on the sample.

Results

Selectivity of O_2 ash rates of photoresist and PMMA

The O_2clean step removes both the photoresist and PMMA, as both are organic materials. Knowing the selectivity is important in order to be able to determine the O_2 ash time in the SA-ALD process (step d in Figure 1).

A bare silicon wafer with either PMMA or S1813 resist was spun on, and the thickness was measured twice using the P-16, Gaertner Ellipsometer, or Filmetrics after a certain amount of O_2 clean time. The results are show in Figure 2 below.
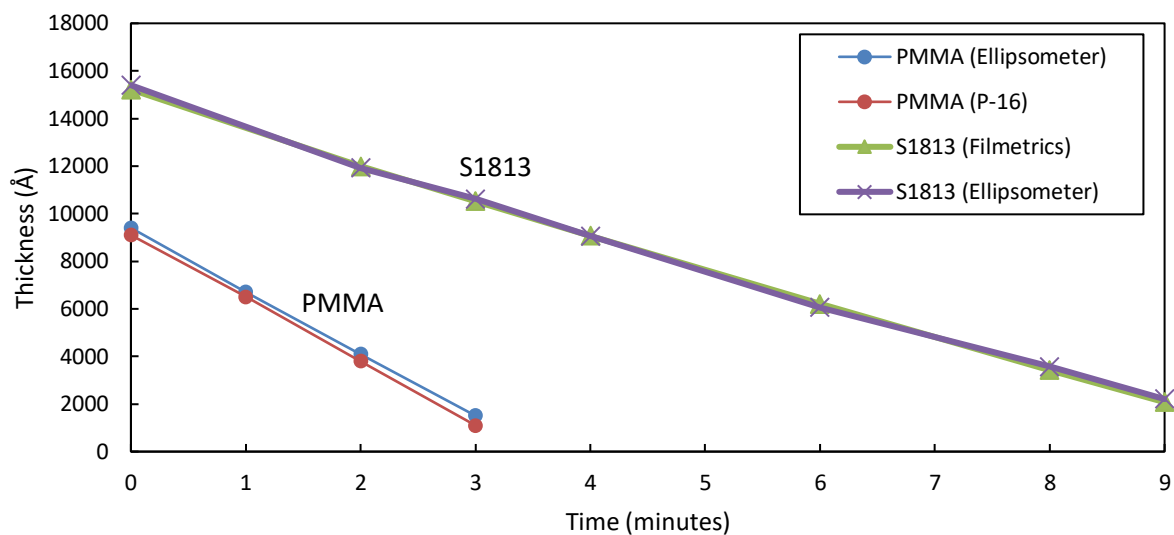
Figure 2. The O$_2$ ash results are shown. PMMA has an etch rate of 2650 Å/min, whereas S1813 has an etch rate of 1450 Å/min. This results in a PMMA:S1813 selectivity of 1.83:1.

While the O$_2$ ash rate of AZ MiR 701 was not tested, it is expected that the ash rate be very similar to S1813.

Contact-Aligner Photolithography Results

Utilizing the 3M test mask and S1813 resist, the following microscope pictures were obtained. This process utilizes the thinned PMMA (estimated thickness ~9400Å) on polymon, S1813 resist, followed by a 5 min O_2 clean. A 1200-loop overnight TiO_2 ALD deposition at 150°C was done. 60-min ultrasonication was used to remove the PMMA. 500-600 Å of TiO_2 is estimated to have been deposited.
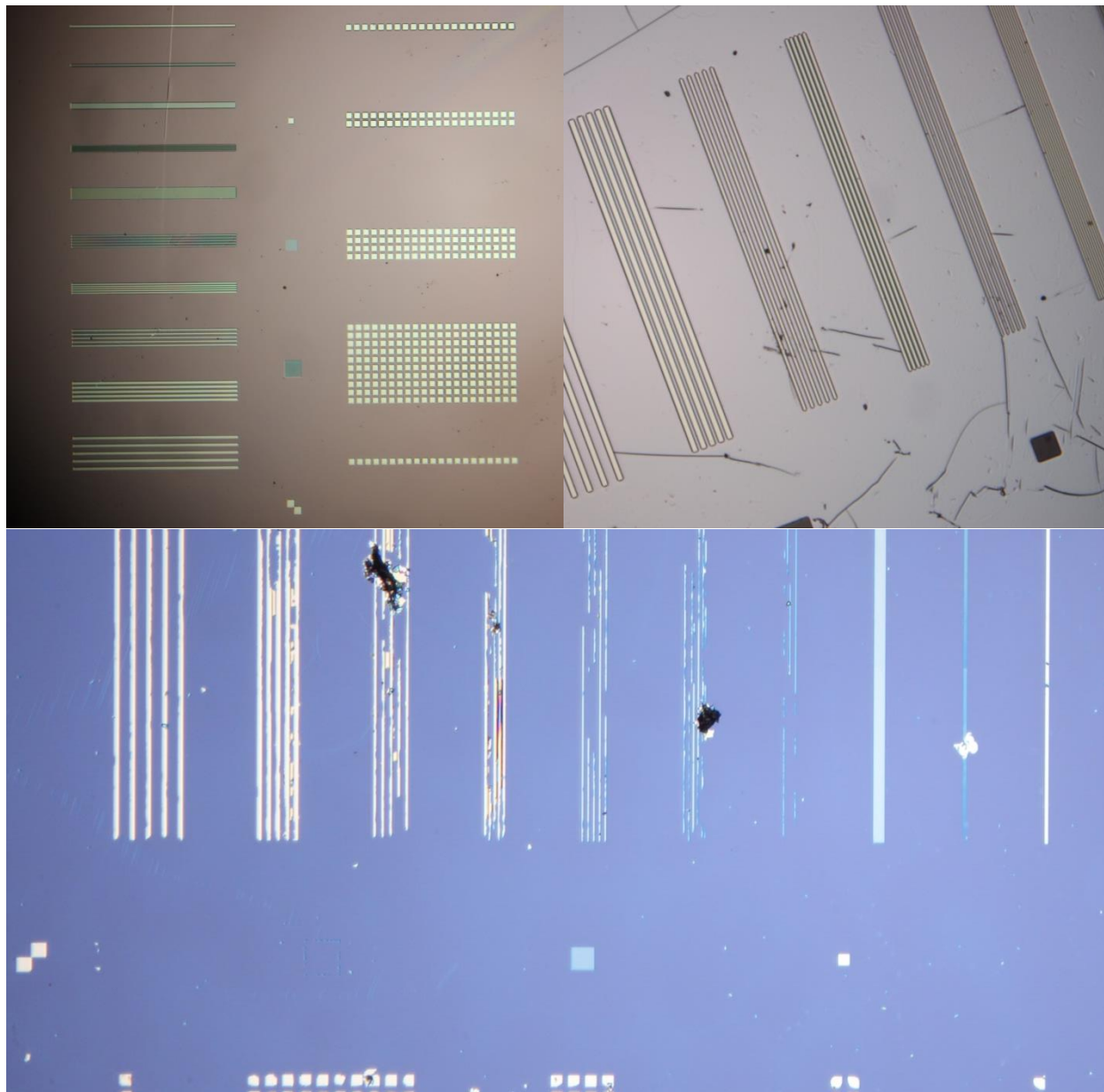

Figure 3. Three stages of an SA-ALD process are shown. The first picture shows the pattern after photoresist removal (a). After a 1200-loop deposition, cracks were found on the PMMA surface (b). Removal of the PMMA layer using ultrasonic agitation reveals a fairly poor pattern transfer (c).
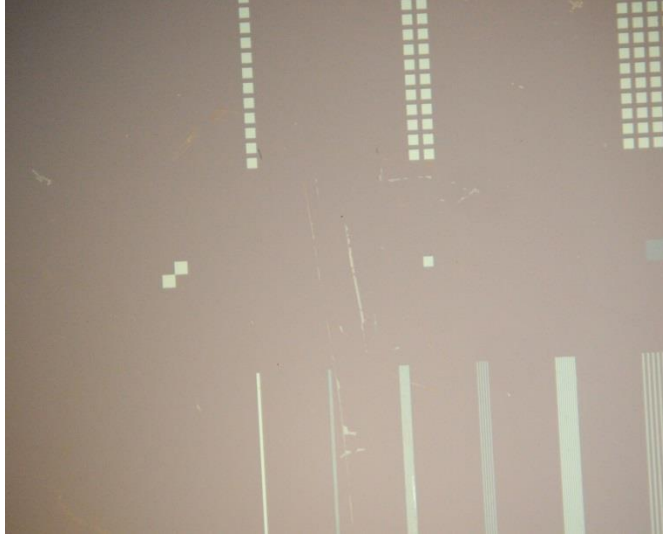
Figure 4. The resulting cleaned wafer after a similar process in Figure 3, but only a 100 loop deposition was performed. This picture shows a bare silicon wafer instead of a polymonitor wafer substrate.

Stepper Photolithography Results

The stepper allows for much smaller features to be patterned. Only polymonitor wafers were used as the substrates, and the super-illumination test reticle was used along with the AZ MiR 701 resist. The results shown are from an FEC with a focus of 0µm and an exposure setting of 225 mJ/cm^2.
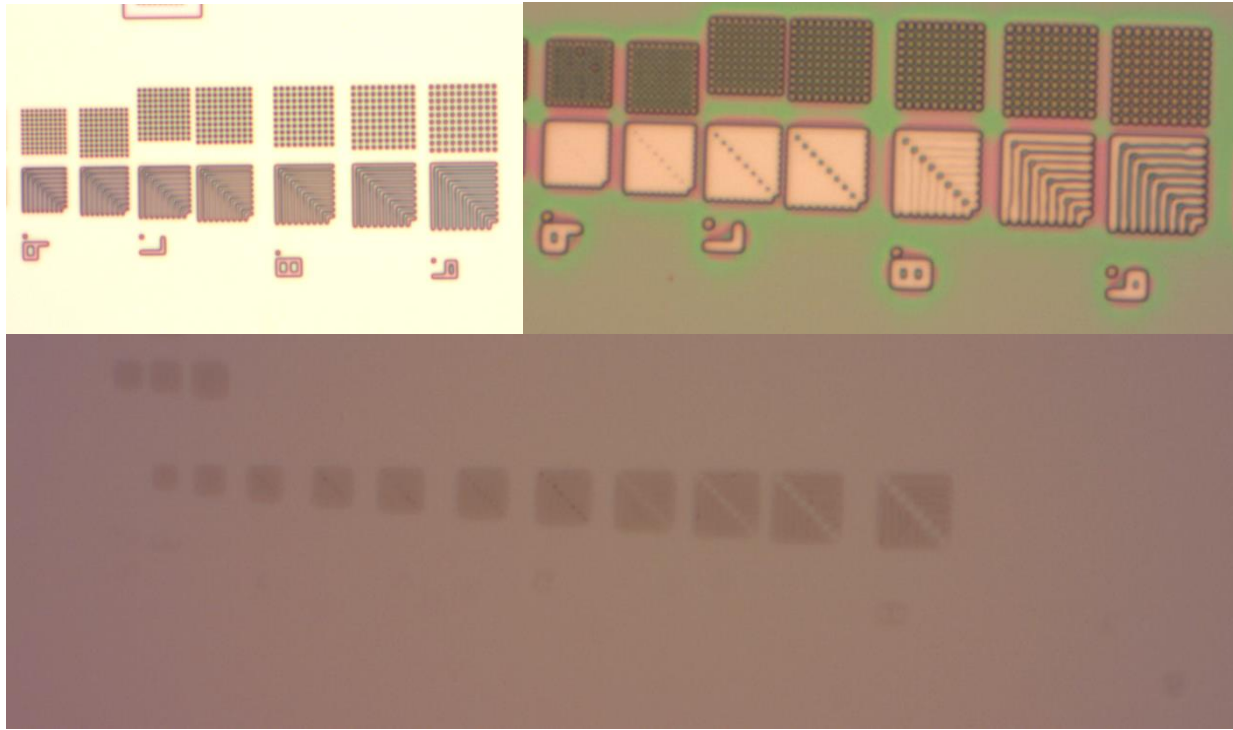

Figure 5. Process snapshots of a bare Si substrate are shown. The patterned resist image is shown in (a), the exposed surface after an 8-minute O_2 clean is shown (b), and the resulting cleaned wafer after a 150-loop deposition is shown (c). The bare Si substrate makes it difficult to see the TiO_2 film.
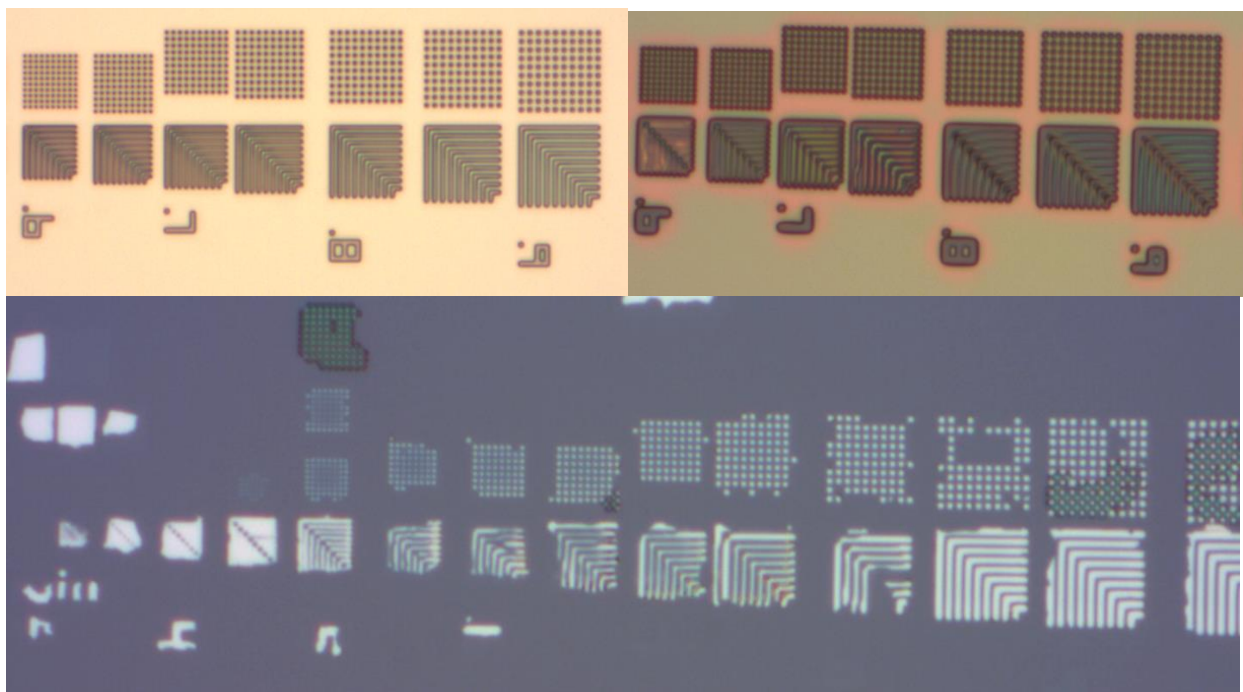
Figure 6. Pattern snapshots in a similar setup to Figure 5 are shown, but with a polymon substrate. In addition, only a 5-minute O_2 clean is used (in contrast to the 8 minutes used for the bare Si substrate). While the contrast high for easy visualization, a similar situation to Figure 3 is shown (poor pattern transfer).
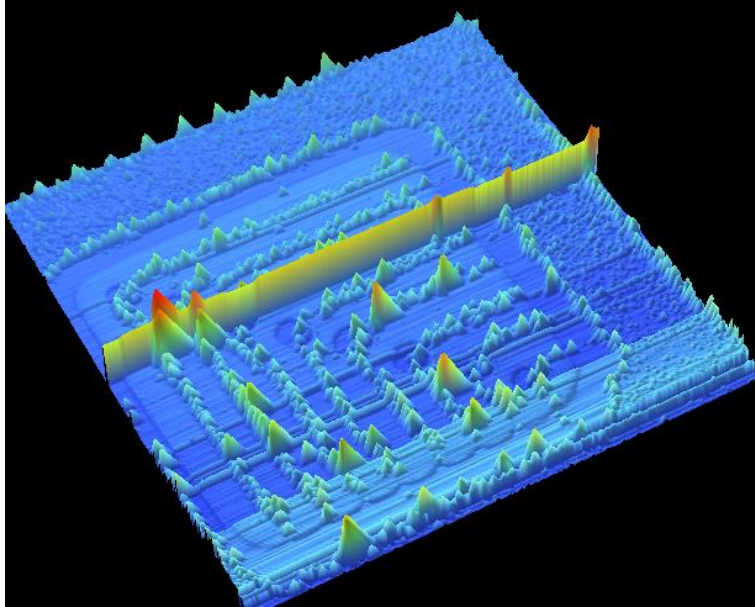
AFM Photos of the cleaned polymon wafers

Figure 7. An AFM photo of one of the elbow-patterns in the super-illumination test reticle is shown. Note the circles that appear at each of the elbow corners, and the smoothness of the substrate between the elbow lines (when compared to the rough outside of the boxed elbow pattern.
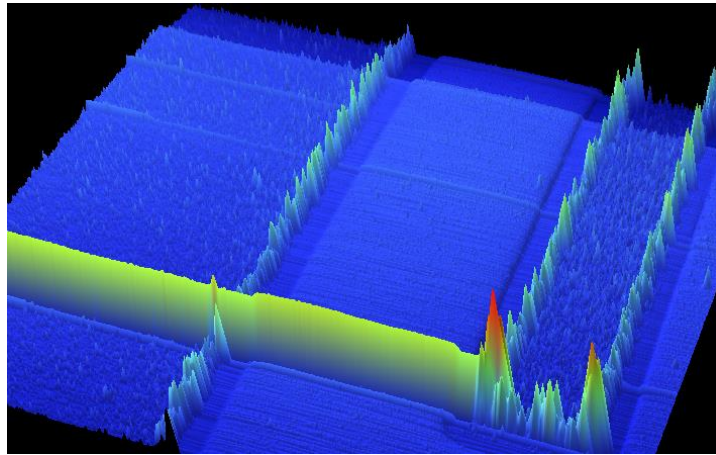

Figure 8. Another AFM photo of a line from the same substrate is shown from Figure 7. Note the smoothness of the ALD film, but the trench and scum that surrounds it. In addition, the film on the outside of the entire pattern is not as smooth as the ALD film in the middle, but slightly rough.
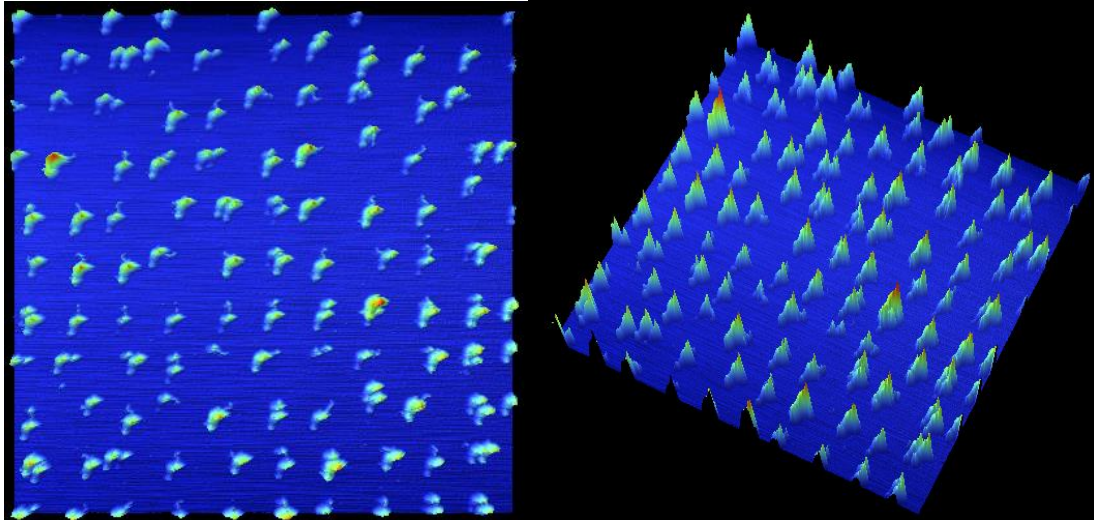
Figure 9. A top-down and isometric view of the dot pattern from the same substrate in Figure 7 and 8 are shown. Note the irregularity of the gridded-dot pattern, and the unevenness of the ALD pillars.
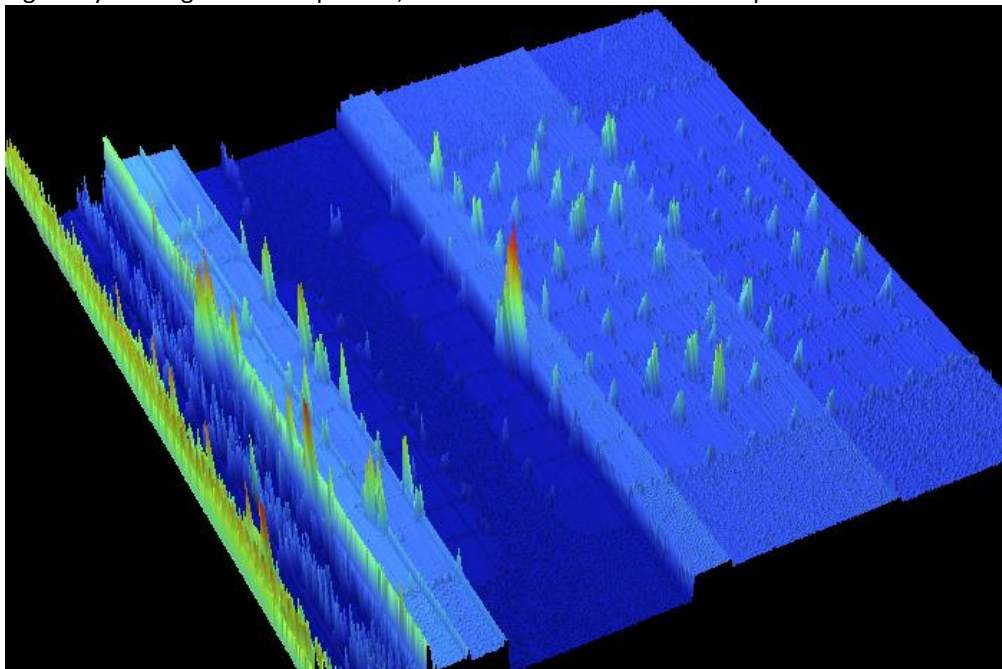

Figure 10. A zoom-in on one of the negative dot patterns from the same substrate. Note the ALD pillars are formed not from the holes, but from the area surrounding the dot patterns. The pillars are due to an over-ashed PMMA film pattern.

Discussion

SA-ALD appears to be feasible with the current tools in the Keller Hall cleanroom, but there are issues that need to be addressed.

Figures 3c and 6c both show relatively poor pattern transfer, even when starting with a relatively good pattern to perform the ALD on (Figures 3a and 6b). This may be due to how the light interacts with the polymon wafer. The thin thermal oxide layer may reflect the light in unexpected ways, and simply using the same determined process parameters from a bare Si substrate might cause the actual PMMA film to not behave as expected.

The FEC for the polymon wafer shows relatively poor patterns for all of the foci and exposures tested, indicating that the problem may not be due to the exposure step. Perhaps the pre-dep hard bake and PMMA film integrity needs to be looked at in further detail, whether through AFM before deposition or by higher resolution microscopy.

In regards to the bare Si substrate, Figure 5c shows that the transferred pattern is clean, and behaves as expected (when compared to Figure 5b). Thus the main problem is in the development of the PMMA pattern after O_2 ashing. 8 minutes was used for the bare Si substrate, but this may have been too much (see Figure 5b's 0.6μm and 0.7μm features).

For long depositions, cracking was seen on the PMMA film (Figure 3b), but was not observed for a shorter deposition (picture not taken, but was for the substrate in Figure 4). The cracking did not seem to affect the quality of the deposition, but perhaps it may have been the source for random ALD dots outside of patterned areas (seen in Figure 3c).

The most curious result is the area surrounding the ALD film, seen in Figures 7 and 8. The smooth trench may be the substrate, but the cause of the discrepancy between that and the "bulk" film is unknown. The random smattering of particle seen in the areas may be residue PMMA, since the PMMA after deposition is removed via ultrasonic agitation in acetone. Little bits and pieces of PMMA may still remain, and it would be interesting to see whether the trenches remain after a quick (~2-3min) O_2 clean in the STS etcher.

Figure 9 shows an interesting result. The positive-image pillars are not arranged in a grid, as expected from the reticle and pre-deposition microscope images. However, the negative-image result from Figure 10 shows it to still be in an orderly pattern.

The only explanation for this is that the ALD film from Figure 9 might be weakly adhered to the surface after ALD deposition. During ultrasonic agitation, perhaps the pillars may have shifted around. While this argument does not exactly hold up to Figure 10's results, one possible explanation for this is that the negative PMMA layer image may have been sharper in Figure 10, preventing PMMA from sneaking under the ALD film and "lifting" it to cause a weaker surface adhesion.

While not shown, one of the biggest issues in the SA-ALD process is the clean-up step. There have been times where a 30-minute O_2 clean after deposition fails to remove the PMMA layer. The only explanation for this is that after the initial O_2 clean to expose the substrate to the ALD precursor gases, a thin layer of photoresist remains on top of the PMMA. This thin layer is enough to cause the ALD film to adhere to the surface still, and the O_2 clean is unable to remove the resulting TiO_2.

This problem was circumvented by putting the sample in an acetone bath, indicating that the side-walls of PMMA did not have ALD film (and thus no photoresist) on them.

Thus the method in cleaning-up the PMMA is uncertain. Should the acetone-bath or the O_2 ash be performed first? This result suggests that the acetone bath be performed first, in order to get rid of a majority of the PMMA. However, visible strands of PMMA are present in the acetone solution, and removing the wafer from the solution can cause the PMMA to adhere back onto the surface, causing scum. This may be the source of the scum seen in Figure 3c, and cannot be removed even after a long time of O_2 ashing.

Conclusion

SA-ALD is feasible within the Keller Hall facilities, but issues in cleaning-up the substrate, finding the optimal process parameters, and extending the usefulness beyond TiO_2 remain unsolved. Performing experiments using TiO_2 as the ALD film are difficult, given the long loop time (~40s) of each loop. If performing experiments under 100 loops, the resulting ALD film is very hard to detect using microscopy, and thus "short" (<1-hour) deposition times should not be performed. It is recommended that further experiments perform ALD-deposition of at least 3 hours.

Notes

I'd like to thank Tony Whipple for his supervision during my time here at the MNC. All of my files (including additional stepper-process and AFM images) for the SA-ALD project are stored on the N drive.

References

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