Diffraction Gradient Pattern Transfer by Nanoimprinting with Photocurable Resist at Room Temperature

Hal Pratt
Advisors: Dr. Helena Gleskova, Dr. Sigurd Wagner
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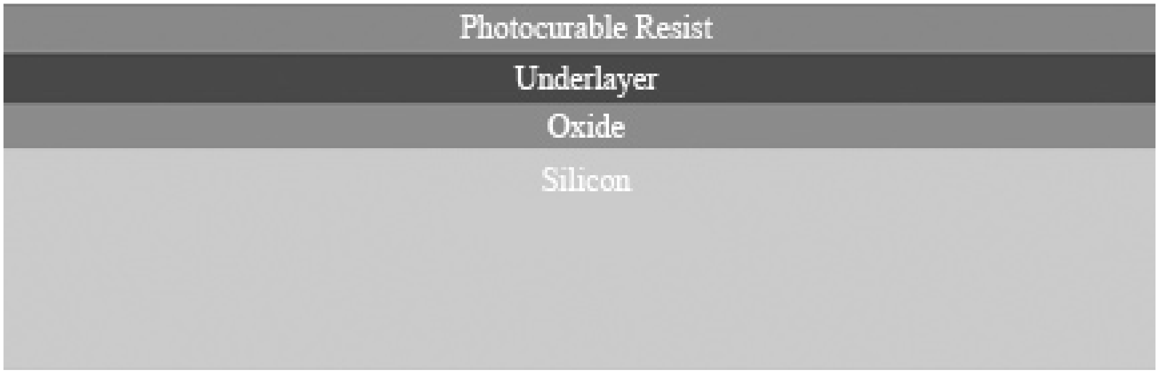
Introduction: Nanoimprinting is a new technology which allows for silicon patterning with a design rule on the scale of nanometers. A mask with the pattern is brought into contact with a silicon wafer coated with resist at high pressure, causing the resist to reproduce the pattern. The resist is then cured, and the mask removed. There are two possible resists that can be used, which are cured differently. The simpler is a thermal resist, which cures when heated. However, with small features, differences in the thermal expansion of the mask and the silicon wafer make this option unteneable. The other option is a photocurable resist, which solidifies when exposed to ultraviolet light. Because this process occurs at room temperature, thermal expansion is not a problem. However, the photocurable resist does not interface well with silicon oxide. This necessitates the use of an intermediate "underlayer" to interface with the oxide and the photocurable resist. In order to transfer the pattern accurately, the photocurable resist must be etched precisely, and then the underlayer must be etched without damaging the photocurable layer. Chromium is then deposited onto the wafer, the resist is lifted off, and the pattern is transferred into the silicon oxide.

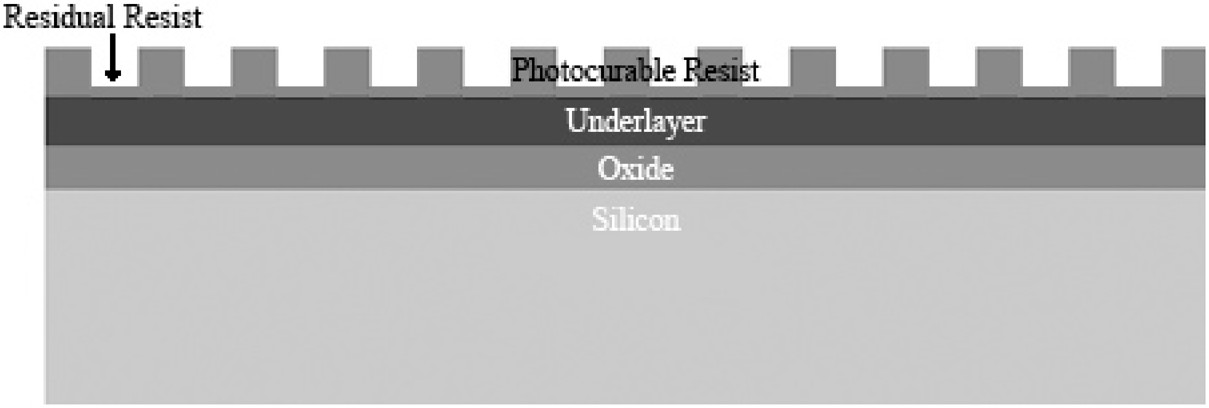
Goal: To develop a reliable process for the transfer of a diffraction gradient pattern from a quartz mask to silicon oxide by nanoimprinting and curing the resist with UV light, based on recipes from Nanonex.

Process: To transfer the pattern into the oxide, a copy of the inverse of the pattern has to be deposited over the oxide of a material which will not be etched by HF. This accomplished by first transferring the pattern into a photo-curable resist. A coat of chromium is then added, and the resist is lifted-off, leaving the chromium pattern. The oxide is then etched away, and then the chromium, leaving the original pattern etched into the oxide. However, because the photo-curable resist does not lift off well, two layers of resist must be used. The pattern is only transferred to the photo-curable layer, so two additional steps are required. First, an etch of the photo-curable removes a small residual amount of resist which is covering the bottom of the depressions in the resist, and second, the underlayer of resist must be etched away.

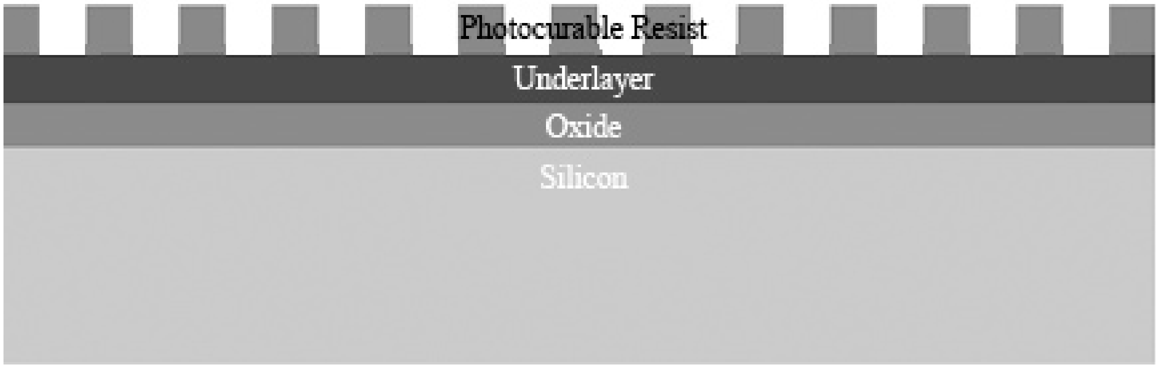
Step 1: The undelayer resist and photocurable resist are spun on.



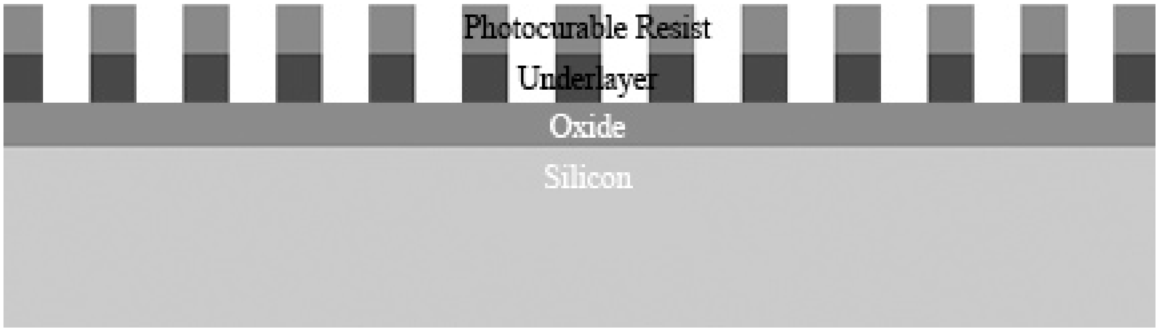
Step 2: The wafer is imprinted, transferring the pattern to the photocurable resist, and leaving a small amount of residual photocurable resist in the patterned areas.



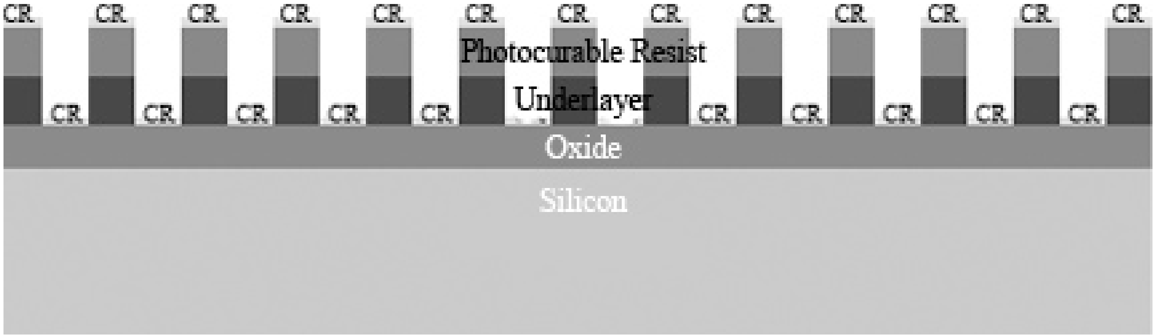
Step 3: The residual resist is etched away with CHF_3 plasma.



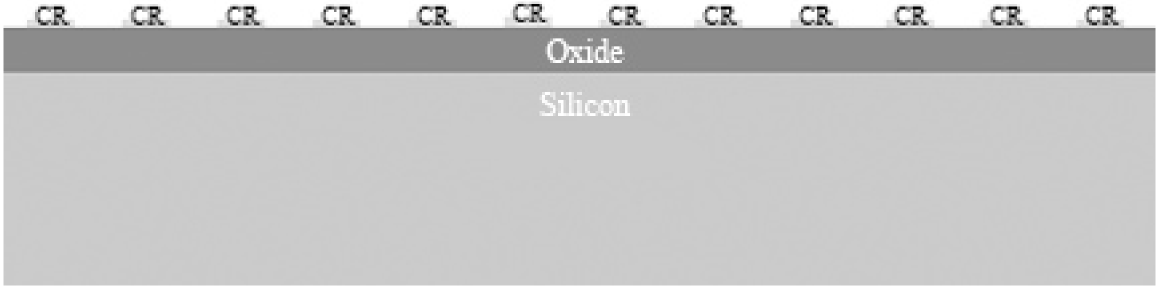
Step 4 : The underlayer is etched by O_2 plasma.



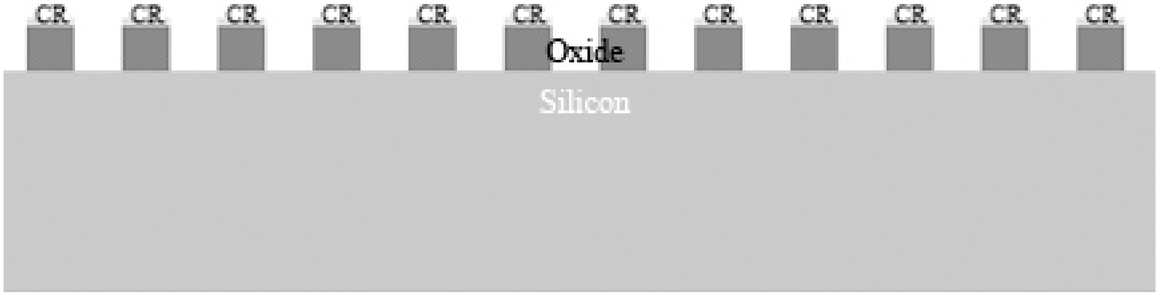
Step 5 : Chromium is deposited over the surface of the wafer.



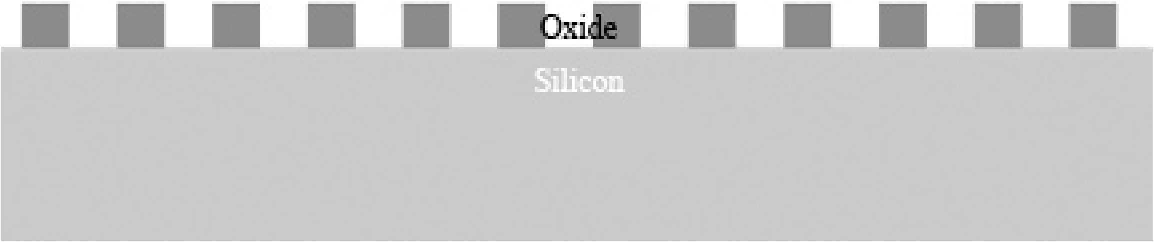
Step 6 : The underlayer is lifted-off, removing the photocurable resist and chromium above it.



Step 7 : The oxide is etched with HF.



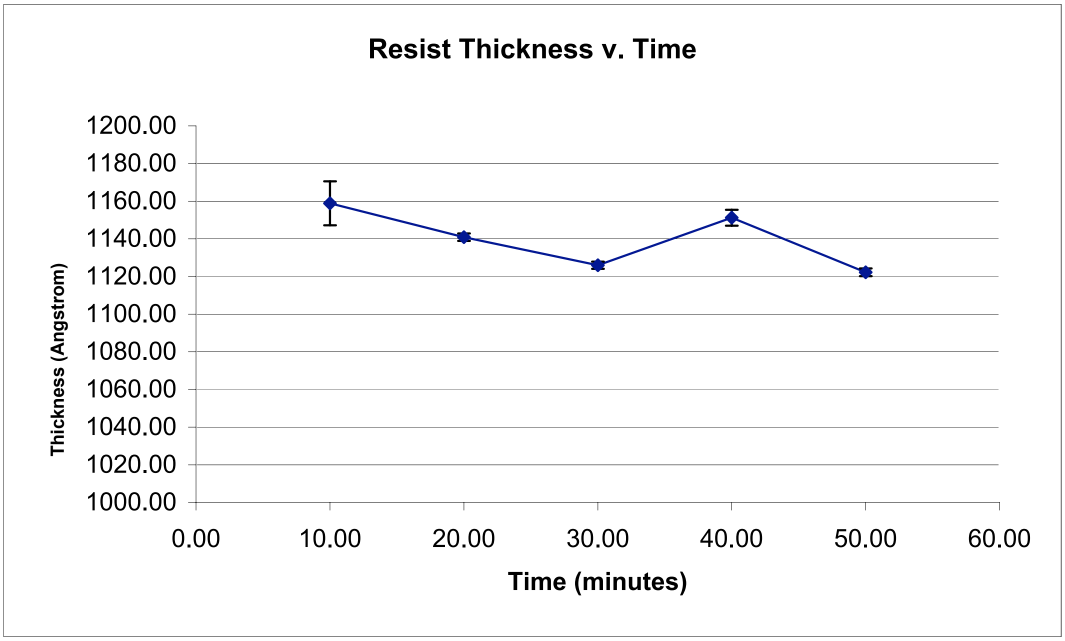
Step 8 : The remaining chromium is etched off.



Experiments:

The first step, the application of the two resists, requires that the thickness of the resists be well controlled so that the amount of material that is to be etched is controlled. The resist thickness is determined by the speed and acceleration of the spin-on process, as well as it's duration. For the underlayer, which must be baked before the photocurable layer can be applied, the duration of the baking time also affects the thickness. The initial recipe suggested by Nanonex was to spin the underlayer on at 4000 rpm for 40 seconds, with an acceleration of 2000 rpm/s, and to bake it for 30 minutes at 95 degrees Celsius.

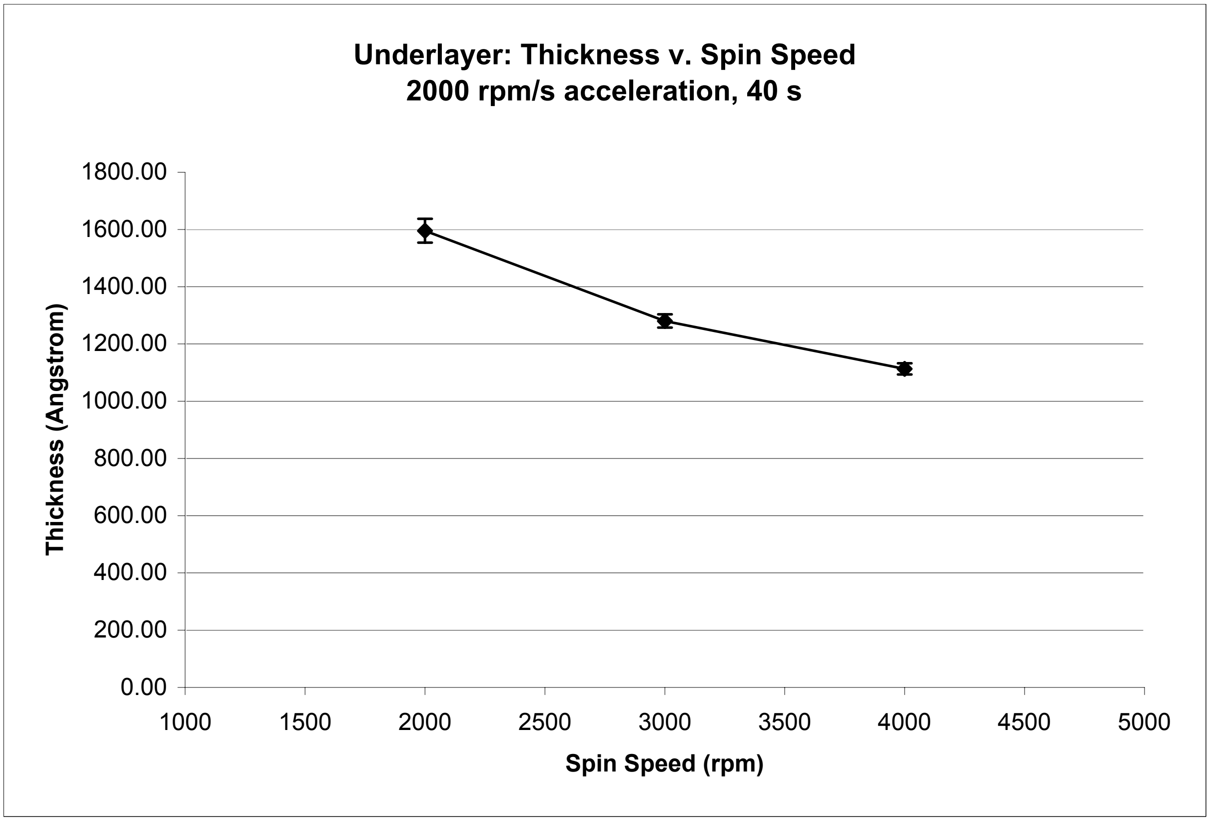
First, the correct baking temperature was determined by spinning resist on at 4000 rpm for 40 seconds, with an acceleration of 2000 rpm/s, then baking the wafer and measuring the thickness of the resist every 10 minutes with an ellipsometer. 17 measurements were made over the surface of the wafer. Before spinning on the resist the wafer was cleaned with acetone, methanol, and propanol, then baked for a minute at 110 degrees to remove water from the surface. This pre-treatment was repeated for every wafer.



The jump in thickness after 40 minutes is not understood; however, the thickness appears to be as thin as possible after approximately 30 minutes, as 20 more minutes of baking does not reduce the thickness. As this agrees with the baking time which Nanonex had suggested, it was decided to use 30 minutes as the standard baking time for the wafer.

Experiments:

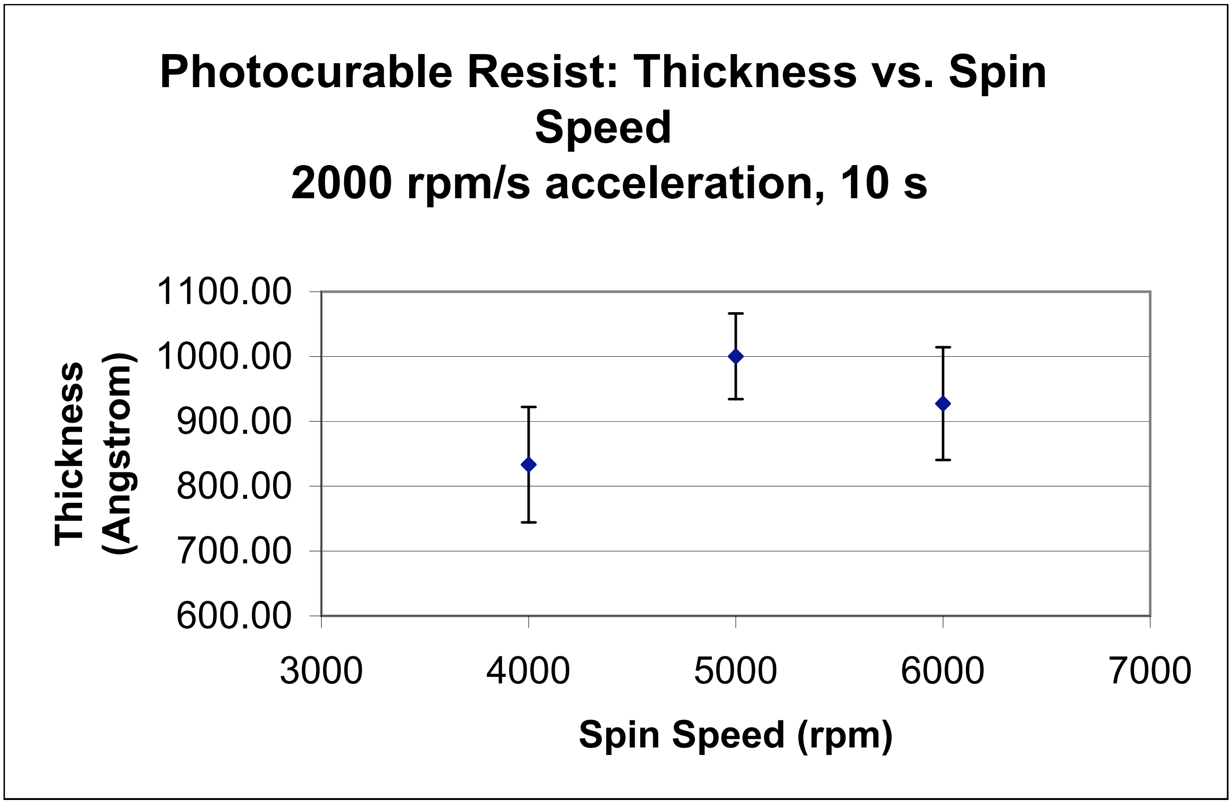
With the baking time established as 30 minutes, the correct spin speed was then determined by spinning the resist on at speeds of 2000, 3000, and 4000 rpm, always with an acceleration of 2000 rpm/s and a duration of 40 seconds. The wafer was then baked for 30 minutes at 95 degrees, and then the thickness was measured with the ellipsometer. Again, 17 measurements were made over the surface of the wafer.



As is expected, the thickness decreases as the spin speed is increased. Speeds above 4000 rpm were not measured because at 4000 rpm the resist is already 110 nm thick, which is acceptably thin, and because of the concentration of resist in solute, the minimum thickness possible, according to Nanonex, is between 100 and 110 nm. It was therefore determined that 4000 rpm would be used as the standard spin speed.

Once the recipe for applying the underlayer was established, the recipe for applying the photocurable layer was determined. The photocurable layer does not require baking before curing, so only the spin speed needed to be established.

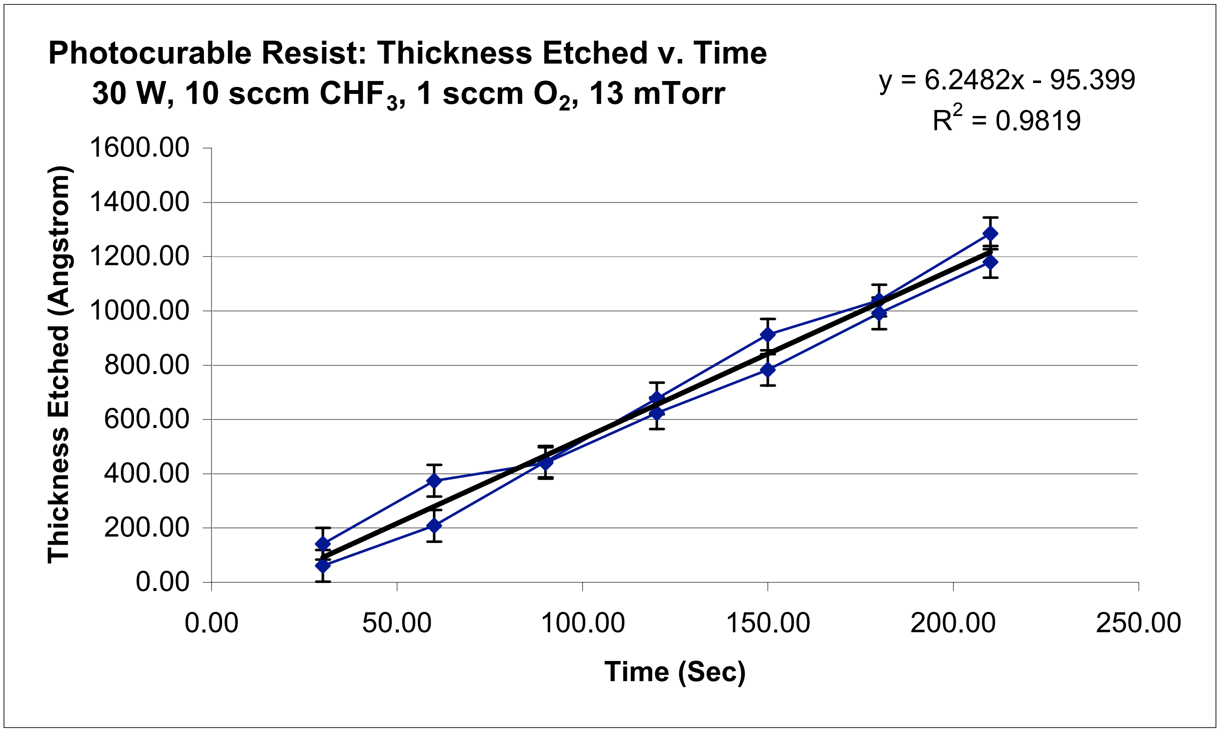
First, underlayer was applied as determined previously, a spin speed of 4000 rpm with an acceleration of 2000 rpm/s and a duration of 40 seconds, followed by a 30 minute bake at 95 degrees. Then the photocurable resist was spun on at 4000 rpm, 5000 rpm, and 6000 rpm, always with an acceleration of 2000 rpm/s, and a duration of 10 seconds. The resist was then imprinted with a blank quartz wafer to cure the resist, but not imprint it with a pattern which would throw off the ellipsometry. The imprinting was done at 20 degrees, with a pressure of 150 psi, and 8 seconds of UV exposure.



These results suggest that the minimum thickness of the resist is encountered at 4000 rpm, and that spinning at higher speeds does not impact the resist's thickness. The greater variation in the thickness measurements of the photocurable layer, in comparison to the underlayer, is because the photocurable resist is much more sensitive to impurities, resulting in a less uniform film. Accordingly, the standard recipe is 4000 rpm, 2000 rpm/s, and 10 seconds of spinning for the photocurable resist.

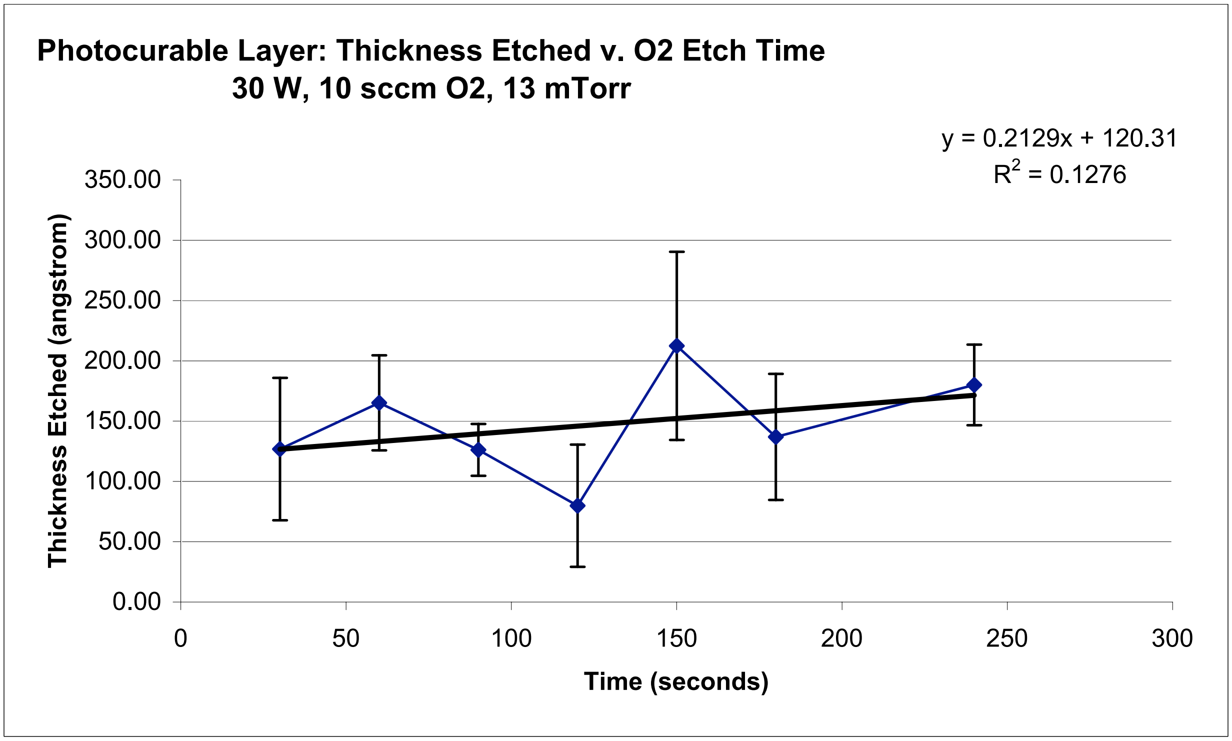
With the recipe for applying the resists determined, the etch rate of both resists had to be determined, in order to determine the duration of the etches. The photocurable layer is designed to be selectively etched with a mixture of O_2 and CHF_3, the amount suggested by Nanonex was 1 sccm of O_2 and 10 sccm of CHF_3. The underlayer is etched by O_2 alone, Nanonex suggested using 10 sccm of O_2. In order to etch cleanly along the pattern made by the imprinting, the pressure was kept as low as possible in the chamber, 13 mTorr for both recipes. Initially, 30 W was used for both recipes. Both resists were etched with both recipes to determine the selectivity of the recipes.

The data was produced by preparing the wafer as described above, and then cleaving it into pieces. Three measurements were made at random points on each shard's surface before etching, and then after etching. The difference of the averages was then plotted. The error bars are the average of the pre- and post-etch standard deviations.

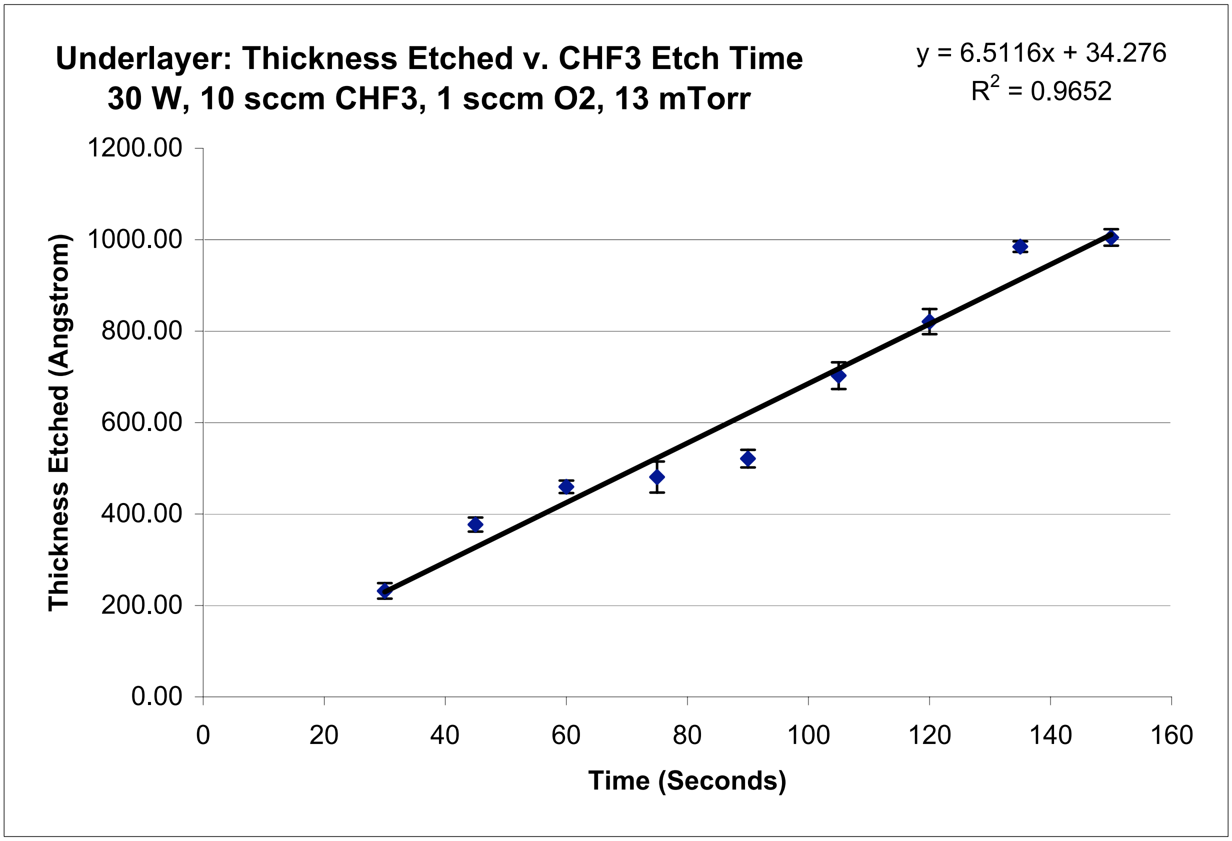


The photocurable resist, which is designed to be etched by CHF3, is seen to have a fairly constant etch rate. The 16 data points were obtained by ramping the etch time up from 30 seconds to 210 seconds, then back down. There was also an etch for 240 seconds; however, at this point, based on the measured thicknesses of the resist above, the underlayer and not the photocurable layer would be etched, and indeed, the point noticeably affected the linear fit, so it was not included.

The etch time is approximately 6 angstrom per second, or about 35 nm per second, with an incubation time of 15 seconds.

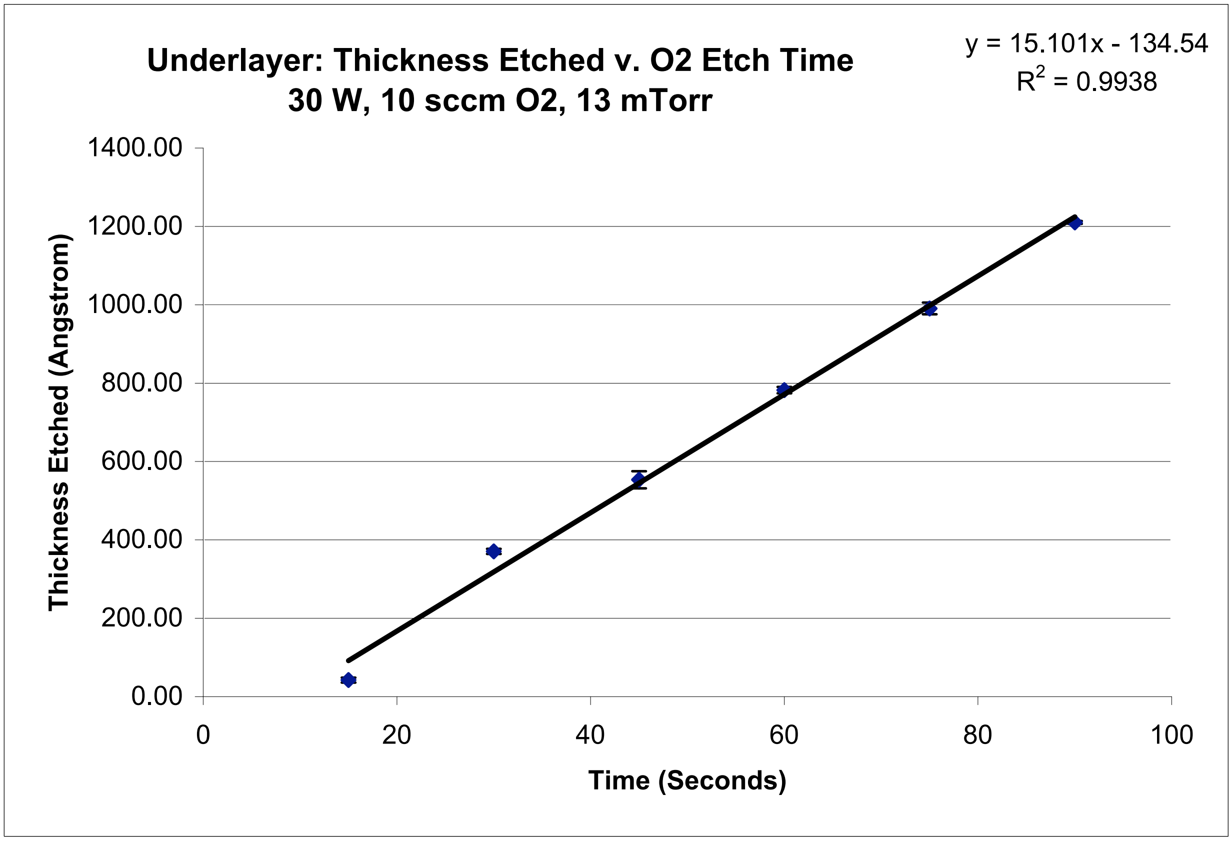


The O2 etch data was developed the same way as the CHF3 data, but with only 8 pieces, and without the ramping back down. As can be seen, the O2, which is not designed to etch the photocurable layer, indeed had almost no effect, and it's affect is, at best, weakly linked to the amount of time the resist is etched. The fact that the thickness of the film is seen to reduce by 10 nm may be either of two factors. First, the O2 might physically bombard the photocurable resist, compressing it. Alternatively, the O2 may slightly change the chemistry at the surface of the CHF3. If the resist's optical properties are not uniform, the ellipsometer measurements are not reliable. The ellipsometer did not register a different index of refraction after etching, so if the second effect is indeed responsible, it cannot have been very severe, and so the above data may be said to reliably demonstrate that neglible etching has occured. If there were significant etching and changes in the optical properties, a time-dependence would be observed.



For the underlayer etches, the same underlayer recipe as developed above is used, but no photocurable layer is applied. The wafer is then cleaved into 8 pieces, and etched with the two recipes.

The CHF3 etch does not appear to be very selective, as the underlayer is etched almost at the same rate as the photocurable resist was. The fact that this curve goes above the origin means that a measurement of the incubation time is impossible; however, since the CHF3 etch time is dictated by the photocurable resist, this isn't a problem.



The O2 etch quickly etches the underlayer away at 15 angstrom a second, almost three times more rapidly than the CHF3 etched, and far faster than the O2 etched the photocurable layer. The incubation time appears to be about 15 seconds,as is expected.

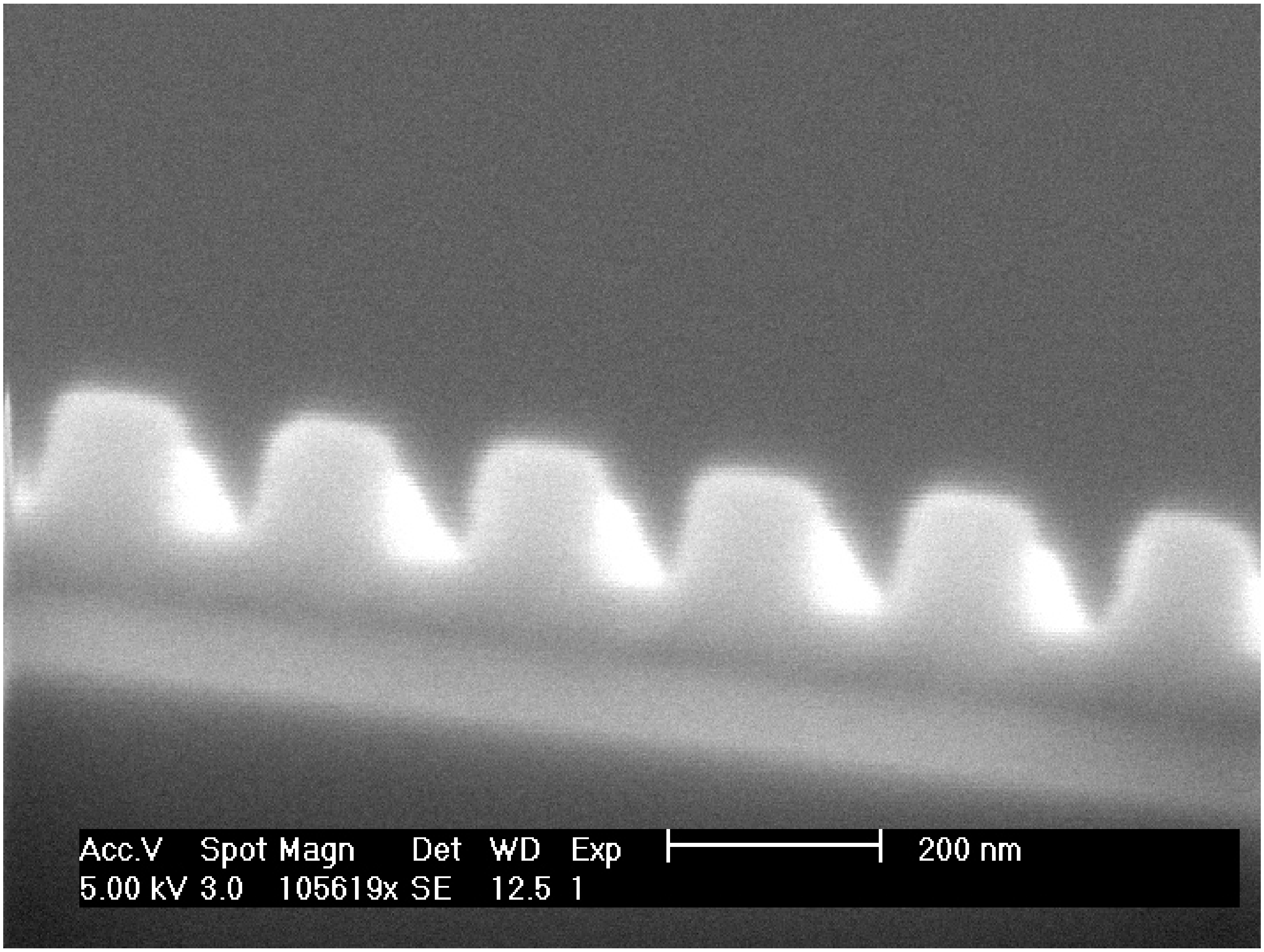
Conclusion:

The CHF3 etch is not very selective, and appears to etch the photocurable layer and underlayer at almost the same rate. This is not a problem; however, the CHF3 etch is meant to remove the residual photocurable resist from the pattern, so if it also etches the underlayer below this, it is not a problem, all that must be insured is that there is enough photocurable resist left that the O2 etch will not etch through it. The O2 etch, conversely, is extremely selective, etching the underlayer much more quickly than CHF3, and hardly, if at all, etching the photocurable layer. This is extremely important, because this ensures that, as long as even a small amount of photocurable resist is left marking the pattern, the underlayer will be etched correctly.

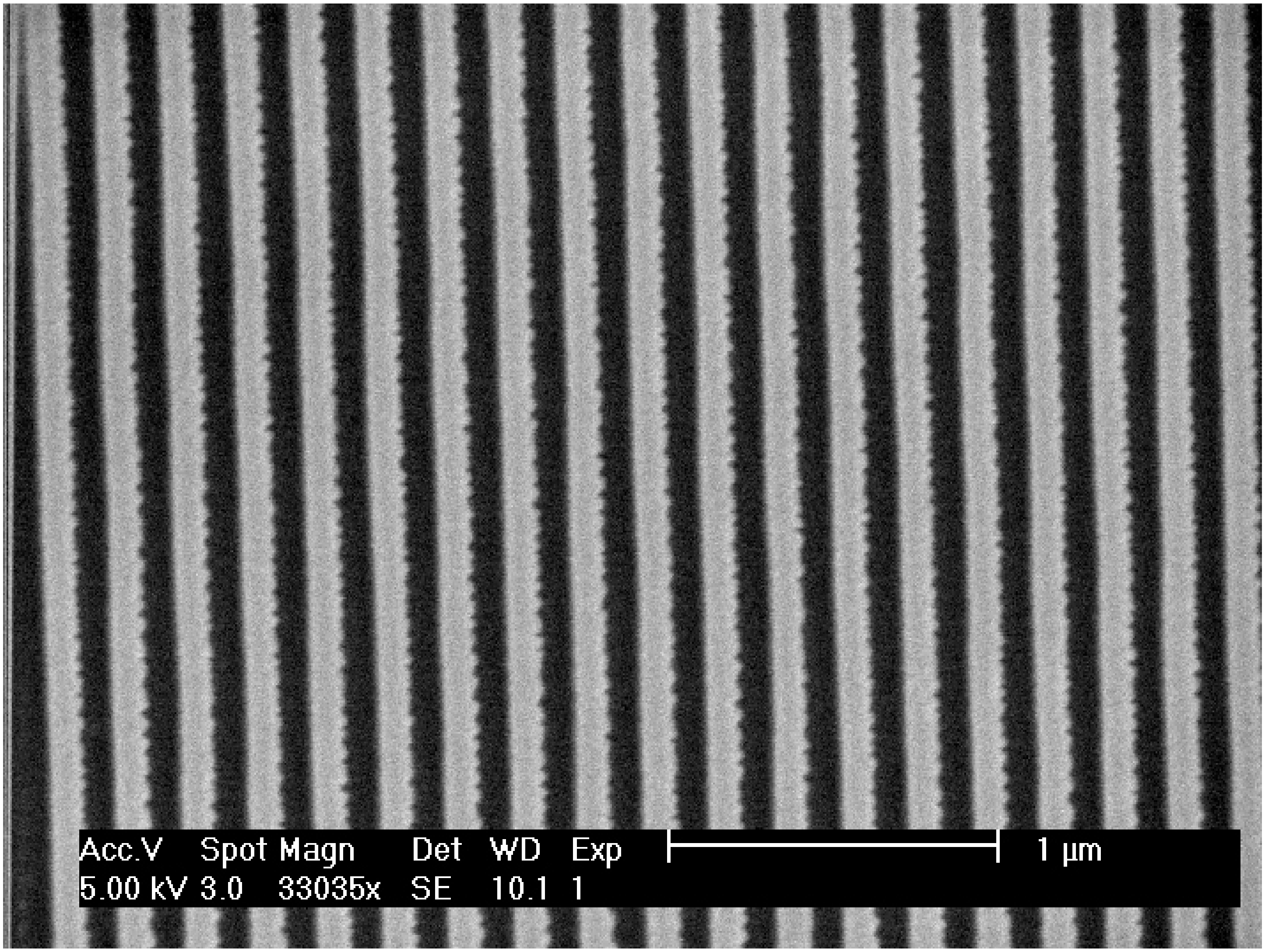
The above experiments suggest what the etch rate for the patterned resist will be, but because it does not have the pattern imprinted, it is possible that imprinting will affect these rates. So wafers were imprinted, using the above established recipes, etched for various times, and then imaged using a SEM.

The nanoimprinter, the Nanonex NX2000, had an 8 second UV exposure time. The temperature was left at room temperature, and the pressure was at 200 psi. This recipe was suggested by Nanonex, and, as seen below, was effective.

This picture shows the imprinted pattern in cross-section before etching:

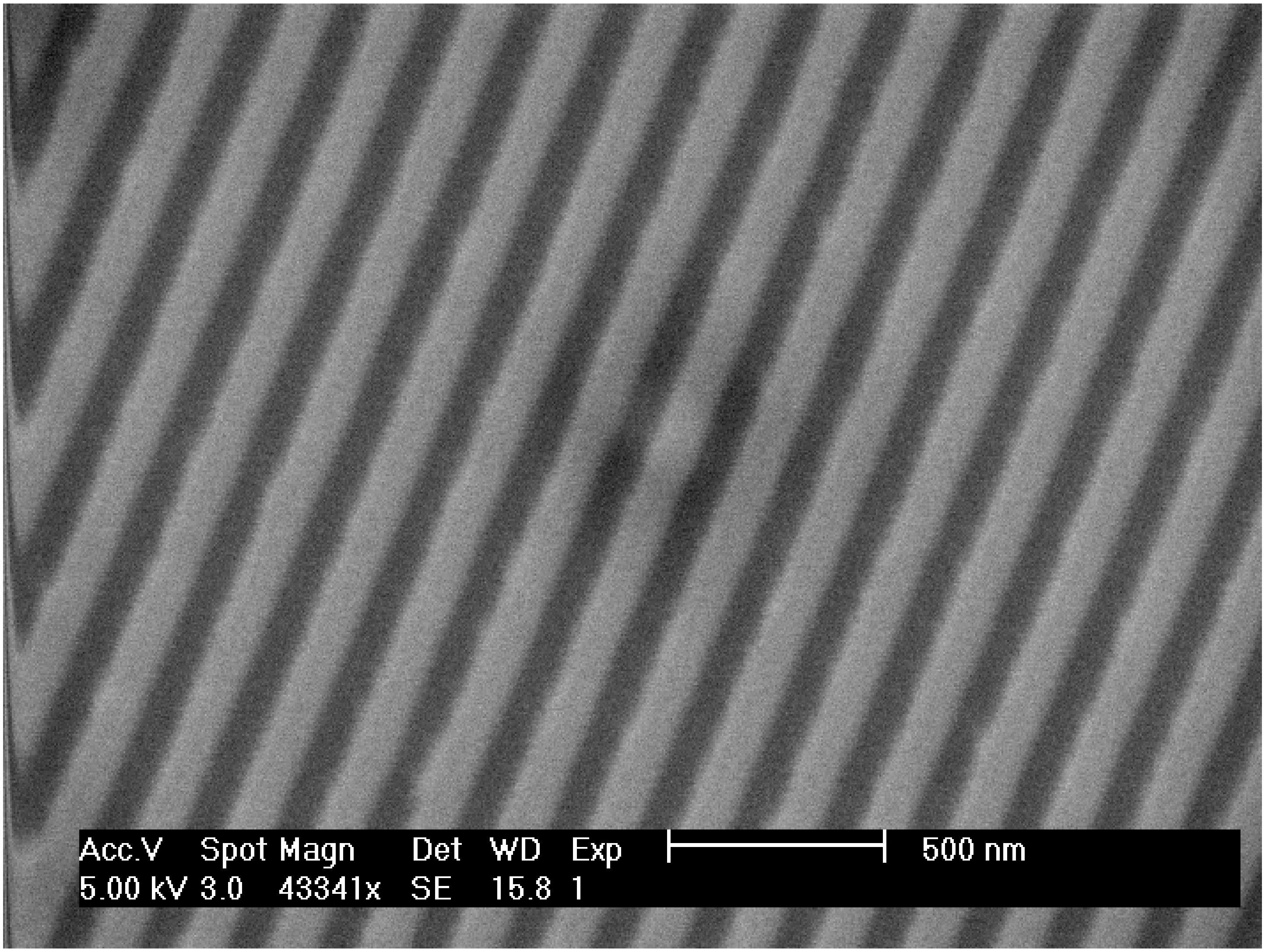


The pattern has transferred into the photoresist cleanly, and there is a distinct interface between the two resists. The pattern is 100 nm deepm with a period of 200 nm. There is about 50 nm of residual resist, and 80 nm of underlayer. The underlayer is slightly thinner than expected, but because the O2 etch is selective, this is not problematic. The picture is not aligned perfectly, so the sidewalls are visible as the brightest area of the image.



This is a top-down view of the pattern, showing that it is uniform across a relatively wide region of the wafer and transfered cleanly. The cause of the asymmetric pattern variations is unknown. But, while the right side of the pattern is significantly more variable than the left side, the variation is not severe.

With the pattern transferred cleanly, the previously determined etching recipe was followed. 30 nm of chromium was then deposited onto the wafer by electron-beam evaporation. The underlayer, and the chromium above it, was then lifted off by a 5:1:1 DIH2O, NH4OH, H2O2 solution at 70° C, which was allowed to sit for 5 minutes. After liftoff, the following image was taken.



The chromium has lifted off cleanly, and the original pattern has been successfully transferred. The final two steps, an oxide etch and a chromium etch, were unable to be completed before my project was over; however, both steps are standard procedures and there is no reason to suspect that they would not work correctly.

Thus, a working recipe for nanoimprinting with a photocurable resist has been established, reliably applying a uniform layer of resist to the silicon, and etching it off at a consistent rate. This recipe is reprinted below:

1 - RCA clean.
2 - Prebake wafer for at least 1 minute at 110° C.
3 - Apply underlayer, spin for 40 s at 4000 rpm with an acceleration of 2000 rpm/s.
4 - Bake at 90° C for 30 minutes.
5 - Apply photocurable resist, spin for 10 s at 4000 rpm with an acceleration of 2000 rpm/s.
6 - Cure resist, 8 s of UV light at room temperature and 200 psi.
7 - Etch with 10 sccm CHF_3, 1 sccm O_2 for 1 minute at 13 mTorr and 30 W.
8 - Etch with 10 sccm O_2 for 1 minute at 13 mTorr and 30 W.
9 - Deposit 30 nm of chromium.
10 - Lift off chromium, 5:1:1: DI H_2O, NH_4OH, H_2O_2, for 5 minutes at 70° C.
11 - Etch oxide.
12 - Etch chromium.

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